

- **ELECTROCHEMISTRY**
- **SURFACE CHEMISTRY**
- **p-BLOCK**

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*THEORY AND EXERCISE BOOKLET*

**CONTENTS**

S.NO.	TOPIC	PAGE NO.
<b>ELECTROCHEMISTRY</b>		
♦	THEORY WITH SOLVED EXAMPLES .....	5 – 34
♦	CLASS ROOM PROBLEMS .....	35 – 41
♦	EXERCISE - I (JEE Main) .....	42 – 50
♦	EXERCISE - II (JEE Advanced – Objective) .....	51 – 55
♦	EXERCISE - III (JEE Advanced) .....	56 – 73
♦	EXERCISE - IV (JEE Advanced – Previous Years).....	74 – 86
♦	ANSWER KEY .....	87 – 89
<b>SURFACE CHEMISTRY</b>		
♦	THEORY WITH SOLVED EXAMPLES .....	90 – 119
♦	EXERCISE - I (JEE Main) .....	120 – 122
♦	EXERCISE - II (JEE Advanced – Objective) .....	123 – 128
♦	EXERCISE - III (JEE Advanced) .....	129 – 131
♦	ANSWER KEY .....	132 – 133
<b>p-BLOCK</b>		
♦	THEORY WITH SOLVED EXAMPLES .....	134 – 171
♦	EXERCISE - I (JEE Main) .....	172 – 178
♦	EXERCISE - II (JEE Advanced – Objective) .....	179 – 185
♦	EXERCISE - III (JEE Advanced) .....	186 – 192
♦	EXERCISE - IV (JEE Main & JEE Advanced – Previous Years).....	193 – 199
♦	ANSWER KEY .....	200

## JEE SYLLABUS

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### • ELECTROCHEMISTRY

#### JEE - ADVANCED

Electrochemical cells and cell reactions; Standard electrode potentials; Nernst equation and its relation to  $G$ ; Electrochemical series, emf of galvanic cells; Faraday's laws of electrolysis; Electrolytic conductance, specific, equivalent and molar conductivity, Kohlrausch's law; Concentration cells.

### • SURFACE CHEMISTRY

#### JEE - ADVANCED

Elementary concepts of adsorption (excluding adsorption isotherms); Colloids: types, methods of preparation and general properties; Elementary ideas of emulsions, surfactants and micelles (only definitions and examples).

### • p-BLOCK

#### JEE - ADVANCED

Preparation and properties of the following compounds: Oxides, peroxides, hydroxides, carbonates, bicarbonates, chlorides and sulphates of sodium, potassium, magnesium and calcium; Boron: diborane, boric acid and borax; Aluminium: alumina, aluminium chloride and alums; Carbon: oxides and oxyacid (carbonic acid); Silicon: silicones, silicates and silicon carbide; Nitrogen: oxides, oxyacids and ammonia; Phosphorus: oxides, oxyacids (phosphorus acid, phosphoric acid) and phosphine; Oxygen: ozone and hydrogen peroxide; Sulphur: hydrogen sulphide, oxides, sulphurous acid, sulphuric acid and sodium thiosulphate; Halogens: hydrohalic acids, oxides and oxyacids of chlorine, bleaching powder; Xenon fluorides.

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**ELECTROCHEMISTRY****Key Concepts****Electrochemical Cells**

An electrochemical cell consists of two electrodes (metallic conductors) in contact with an electrolyte (an ionic conductor).

An electrode and its electrolyte comprise an **Electrode Compartment**.

Electrochemical Cells can be classified as:

**(i) Electrolytic Cells** in which a non-spontaneous reaction is driven by an external source of current.

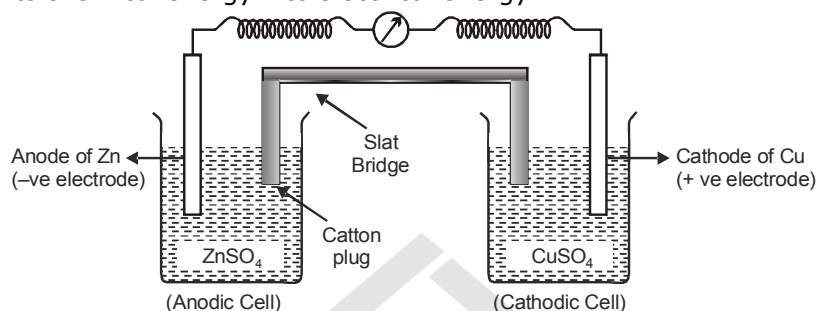
**(ii) Galvanic Cells** which produce electricity as a result of a spontaneous cell reaction.

**Note:** In a **galvanic cell**, cathode is positive with respect to anode.

In a **electrolytic cell**, anode is made positive with respect to cathode.

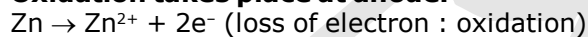
**GALVANIC CELL**

This cell converts chemical energy into electrical energy.

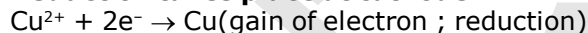


Galvanic cell is made up of two half cells i.e., anodic and cathodic. The cell reaction is of redox kind. Oxidation takes place at anode and reduction at cathode. It is also known as **voltaic cell**. It may be represented as shown in Fig. Zinc rod immersed in  $\text{ZnSO}_4$  behaves as anode and copper rod immersed in  $\text{CuSO}_4$  behaves as cathode.

**Oxidation takes place at anode.**



**Reduction takes place at cathode:**



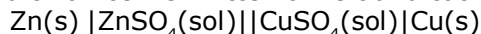
**Overall process :**  $\text{Zn(s)} + \text{Cu}^{2+} \rightarrow \text{Cu(s)} + \text{Zn}^{2+}$

In galvanic cell like Daniell cell: electrons flow from anode (zinc rod) to the cathode (copper rod) through external circuit; zinc dissolves as  $\text{Zn}^{2+}$ ;  $\text{Cu}^{2+}$  ion in the cathode cell picks up two electron and become deposited at cathode.

**REPRESENTATION OF A CELL (IUPAC CONVENTIONS):**

Let us illustrate the convention taking the example of Daniel cell.

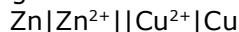
(i) Anodic half cell is written on left and cathodic half cell on right hand side.



(ii) Two half cells are separated by double vertical lines: Double vertical lines indicate salt bridge or any type of porous partition.

(iii) EMF (electromotive force) may be written on the right hand side of the cell.

(iv) Single vertical lines indicate the phase separation between electrode and electrolyte solution.



(v) Inert electrodes are represented in the bracket

**RELATIONSHIP BETWEEN  $\Delta G$  AND ELECTRODE POTENTIAL**

Let  $n$ , faraday charge is taken out from a cell of e.m.f. ( $E$ ) then electrical work done by the cell may be calculated as,

$$\text{Work done} = \text{Charge} \times \text{Potential} = nFE$$

From thermodynamics we know that decrease in Gibbs free energy of a system is a measure of reversible or maximum obtainable work by the system if there is no work due to volume expansion

$$\therefore \Delta G = -nFE$$

$$\text{Under standard state } \Delta G^\circ = -nFE^\circ \dots\dots\dots(1)$$

(i) From thermodynamics we know,  $\Delta G$  = negative for spontaneous process. Thus from eq. (i) it is clear that the EMF should be +ve for a cell process to be feasible or spontaneous.

- (ii) When  $\Delta G$  = positive,  $E$  = negative and the cell process will be non spontaneous.

Reactions	$\Delta G$	$E$
Spontaneous	(-)	(+)
Non-spontaneous	(+)	(-)
Equilibrium	0	0

Standard free energy change of a cell may be calculated by electrode potential data.

Substituting the value of  $E^0$  (i.e., standard reduction potential of cathode-standard reduction potential of anode) in eq. (i) we may get  $\Delta G^0$ .

### CONCEPT OF ELECTROMOTIVE FORCE (EMF) OF A CELL

Electron flows from anode to cathode in external circuit due to a pushing effect called or electromotive force (e.m.f.). EMF is called as cell potential. Unit of e.m.f. of cell is volt.

EMF of cell may be calculated as:

$E_{\text{cell}} = \text{reduction potential of cathode} - \text{Reduction potential of anode}$

Similarly, standard e.m.f. of the cell ( $E^0$ ) may be calculated as

$E^0_{\text{cell}} = \text{Standard reduction potential of cathode} - \text{Standard reduction potential of anode.}$

### SIGN CONVENTION OF EMF

EMF of cell should be positive other wise it will not be feasible in the given direction.

$\text{Zn}   \text{ZnSO}_4    \text{CuSO}_4   \text{Cu}$	$E = + 1.10 \text{ volt (Feasible)}$
$\text{Cu}   \text{CuSO}_4    \text{ZnSO}_4   \text{Zn}$	$E = - 1.10 \text{ volt (Not Feasible)}$

### SALT BRIDGE

Two electrolyte solutions in galvanic cells are separated using salt bridge as represented in the Fig. Salt bridge is a device to minimize or eliminate the liquid junction potential. Saturated solution of salt like KCl,  $\text{KNO}_3$ ,  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{NO}_3$  etc. in agar-agar gel is used in salt bridge. Salt bridge contains high concentration of ions viz.  $\text{K}^+$  and  $\text{NO}_3^-$  at the junction with electrolyte solution. Thus, salt bridge carries whole of the current across the boundary; more over the  $\text{K}^+$  and  $\text{NO}_3^-$  ions have same speed. Hence, salt bridge with uniform and same mobility of cations and anions completes the electrical circuit & permits the ions to migrate.

### NERNST EQUATION

Walter nernst derived a relation between cell potential and concentration or Reaction quotient.

$$\Delta G = \Delta G^0 + RT \ln Q \quad \dots\dots\dots(i)$$

where  $\Delta G$  and  $\Delta G^0$  are free energy and standard free energy change, 'Q' is reaction quotient.

$$\therefore -\Delta G = nFE \quad \text{and} \quad -\Delta G^0 = nFE^0$$

Thus from Eq. (i), we get  $-nFE = -nFE^0 + RT \ln Q$

$$\text{At } 25^\circ\text{C, above equation may be written as } E = E^0 - \frac{0.0591}{n} \log Q$$

Where 'n' represents number of moles of electrons involved in process.

$E$ ,  $E^0$  are e.m.f. and standard e.m.f. of the cell respectively.

In general, for a redox cell reaction involving the transference of  $n$  electrons

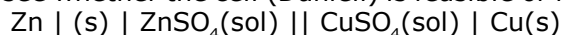
$aA + bB \rightarrow cC + dD$ , the EMF can be calculated as:

$$E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

### THERMODYNAMIC TREATMENT OF NERNST EQUATION

#### (i) Prediction and feasibility of spontaneity of a cell reaction.

Let us see whether the cell (Daniell) is feasible or not; i.e. whether Zinc will displace copper or not.



$$E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ volt} ; E^0_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ volt}$$

$$E^0_{\text{cell}} = E^0_{\text{Cu}^{2+}/\text{Cu}} - E^0_{\text{Zn}^{2+}/\text{Zn}}$$

$$= 0.34 - (-0.76) = + 1.10 \text{ volt}$$

Since  $E^0 = + \text{ve}$ , hence the cell will be feasible and zinc will displace copper from its salt solution. In the other words zinc will reduce copper.

(ii) **Determination of equilibrium constant :** We know, that

$$E = E^0 - \frac{0.0591}{n} \log Q \quad \dots\dots\dots(1)$$

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e.  $E = 0$

$\therefore$  From Eq. (i), we have

$$0 = E^0 - \frac{0.0591}{n} \log K_{eq} \quad \text{or } K_{eq} = \text{anti log} \left[ \frac{nE^0}{0.0591} \right]$$

(iii) **Heat of Reaction inside the cell :** Let  $n$  Faraday charge flows out of a cell of e.m.f.  $E$ , then

$$-\Delta G = nFE \quad \dots\dots\dots(i)$$

Gibbs Helmholtz equation (from thermodynamics) may be given as,

$$\Delta G = \Delta H + T \left[ \frac{\partial \Delta G}{\partial T} \right]_p \quad \dots\dots\dots(ii)$$

From Eqs. (i) and (ii), we have

$$-nFE = \Delta H + T \left[ \frac{\partial (-nFE)}{\partial T} \right]_p = \Delta H - nFT \left[ \frac{\partial E}{\partial T} \right]_p$$

$$\therefore \Delta H = -nFE + nFT \left[ \frac{\partial E}{\partial T} \right]_p$$

(iv) **Entropy change inside the cell :** We know that  $G = H - TS$  or  $\Delta G = \Delta H - T\Delta S$  .....(i) where

$\Delta G$  = Free energy change ;  $\Delta H$  = Enthalpy change and  $\Delta S$  = entropy change.

According to Gibbs Helmholtz equation,

$$\Delta G = \Delta H + T \left[ \frac{\partial \Delta G}{\partial T} \right]_p \quad \dots\dots\dots(ii)$$

From Eqs. (i) and (ii), we have

$$-T\Delta S = T \left[ \frac{\partial \Delta G}{\partial T} \right]_p \quad \text{or } \Delta S = - \left[ \frac{\partial \Delta G}{\partial T} \right]_p$$

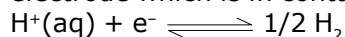
$$\text{or } \Delta S = nF \left[ \frac{\partial E}{\partial T} \right]_p$$

where  $\left[ \frac{\partial E}{\partial T} \right]_p$  is called temperature coefficient of cell e.m.f.

### **DIFFERENT TYPES OF HALF-CELLS AND THEIR REDUCTION POTENTIAL**

#### **(1) Gas - Ion Half Cell :**

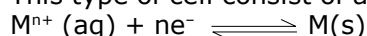
In such a half cell, an inert collector of electrons, platinum or graphite is in contact with gas and a solution containing a specified ion. One of the most important gas-ion half cell is the hydrogen-gas-hydrogen ion half cell. In this cell, purified  $H_2$  gas at a constant pressure is passed over a platinum electrode which is in contact with an acid solution.



$$E_{H^+/H_2} = E_{H^+/H_2}^0 - \frac{0.0591}{1} \log \frac{(pH_2)^{1/2}}{[H^+]}$$

#### **(2) Metal-Metal Ion Half Cell :**

This type of cell consist of a metal  $M$  is contact with a solution containing  $M^{n+}$  ions.



$$E_{M^{n+}/M} = E_{M^{n+}/M}^0 - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

**(3) Metal-Insoluble Salt-Anion Half Cell :**

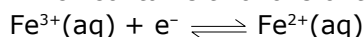
In this half cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. eg. Silver-Silver Chloride Half Cell :

This half cell is represented as  $\text{Cl}^-/\text{AgCl}/\text{Ag}$ . The equilibrium reaction that occurs at the electrode is  $\text{AgCl(s)} + \text{e}^- \rightleftharpoons \text{Ag(s)} + \text{Cl}^-(\text{aq})$

$$E_{\text{Cl}^-/\text{AgCl}/\text{Ag}} = E_{\text{Cl}^-/\text{AgCl}/\text{Ag}}^0 - \frac{0.0591}{1} \log [\text{Cl}^-], \quad E_{\text{Ag}^+/\text{Ag}}^0 + \frac{0.059}{1} \log \frac{(K_{\text{sp}})}{[\text{Cl}^-]} \text{AgCl}$$

**(4) Oxidation-reduction Half Cell :**

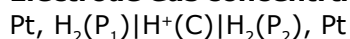
This type of half cell is made by using an inert metal collector, usually platinum, immersed in a solution which contains two ions of the same element in different states of oxidation. eg.  $\text{Fe}^{2+} - \text{Fe}^{3+}$  half cell.



$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - \frac{0.0591}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

**CONCENTRATION CELL**

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell.

**(i) Electrode Gas concentration cell :**

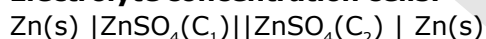
Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.

Cell Process :  $1/2 \text{H}_2(\text{p}_1) \rightarrow \text{H}^+(\text{c}) + \text{e}^-$  (Anode process)

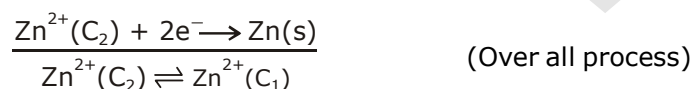
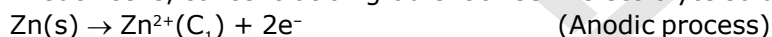
$$\frac{\text{H}^+(\text{c}) + \text{e}^- \rightarrow 1/2 \text{H}_2(\text{p}_2)}{1/2 \text{H}_2(\text{p}_1) \rightleftharpoons 1/2 \text{H}_2(\text{p}_2)} \quad \therefore \quad E = - \frac{2.303RT}{F} \log \left[ \frac{\text{p}_2}{\text{p}_1} \right]^{1/2}$$

$$\text{or} \quad E = - \left[ \frac{2.303RT}{2F} \right] \log \left[ \frac{\text{p}_2}{\text{p}_1} \right], \quad \text{At } 25^\circ\text{C}, E = - \frac{0.059}{2F} \log \left[ \frac{\text{p}_2}{\text{p}_1} \right]$$

For spontaneity of such cell reaction  $\text{p}_1 > \text{p}_2$

**(2) Electrolyte concentration cells:**

In such cells, concentration gradient arise in electrolyte solutions. Cell process may be given as,



$\therefore$  From Nernst equation, we have

$$E = 0 - \frac{2.303RT}{2F} \log \left[ \frac{\text{C}_1}{\text{C}_2} \right] \quad \text{or} \quad E = \frac{2.303RT}{2F} \log \left[ \frac{\text{C}_2}{\text{C}_1} \right]$$

For spontaneity of such cell reaction,  $\text{C}_2 > \text{C}_1$ .

**COMMERCIAL VOLTAGE CELLS**

Batteries can be classified as primary and secondary. Primary batteries can not be returned to their original state by recharging, so when the reactants are consumed, the battery is "dead" and must be discarded. Secondary batteries are often called storage batteries or rechargeable batteries. The



reactions in these batteries can be reversed; thus, the batteries can be recharged.

### PRIMARY BATTERIES:

#### DRY CELLS AND ALKALINE BATTERIES

Zinc serves as the anode, and the cathode is a graphite rod placed down the center of the device. These cells are often called "dry cells" because there is no visible liquid phase. However, water is present, so the cell contains a moist paste of  $\text{NH}_4\text{Cl}$ ,  $\text{ZnCl}_2$  and  $\text{MnO}_2$ . The moisture is necessary because the ions present must be in a medium in which they can migrate from one electrode to the other. The cell generates a potential of 1.5 V using the following half-reactions.

Cathode, reductions :  $2\text{NH}_4^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{NH}_3(\text{g}) + \text{H}_2(\text{g})$

Anode, oxidation :  $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$

The two gases formed at the cathode will build up pressure and could cause the cell to rupture. This problem is avoided, however, by two other reactions that take place in the cell. Ammonia molecules bind to  $\text{Zn}^{2+}$  ions, and hydrogen gas is oxidized by  $\text{MnO}_2$  to water.

$\text{Zn}^{2+}(\text{aq}) + 2\text{NH}_3(\text{g}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{Zn}(\text{NH}_3)_2\text{Cl}_2(\text{s})$

$2\text{MnO}_2(\text{s}) + \text{H}_2(\text{g}) \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\text{l})$

LeClanche cells were widely used because of their low cost, but they have several disadvantages. If current is drawn from the battery rapidly, the gaseous products cannot be consumed rapidly enough, so the cell resistance rises, and the voltage drops. In addition, the zinc electrode and ammonium ions are in contact in the cell, and these chemicals react slowly.

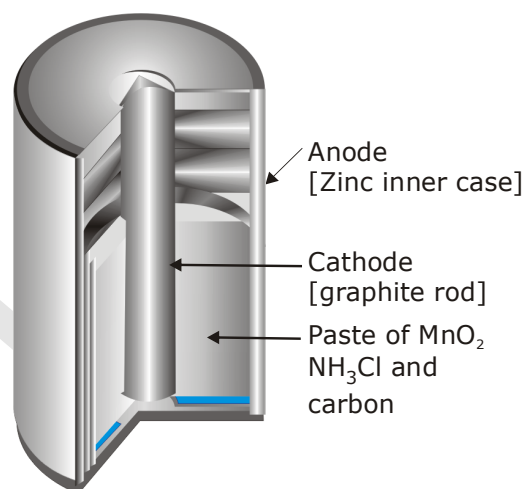
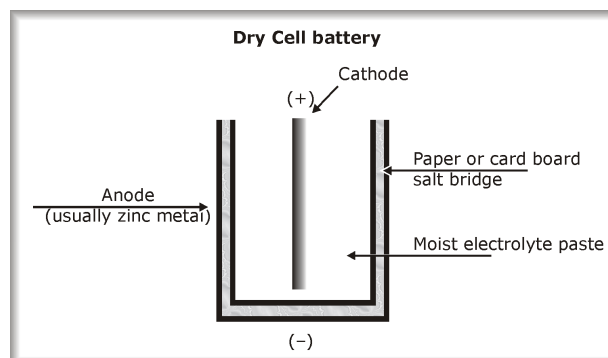
Recall that zinc reacts with acids to form hydrogen. The ammonium ion,  $\text{NH}_4^+(\text{aq})$ , is a weak Bronsted acid and reacts slowly with zinc. Because of this reaction, these voltaic cells cannot be stored indefinitely. When the zinc outer shell deteriorates, the battery can leak acid and perhaps damage the appliance in which it is contained.

At the present time **alkaline batteries** are used the chemistry of alkaline cells is quite similar to that in a LeClanche cell, except that the material inside the cell is basic (alkaline). Alkaline cells use the oxidation of zinc and the reduction of  $\text{MnO}_2$  to generate a current, but  $\text{NaOH}$  or  $\text{KOH}$  is used in the cell instead of the acidic salt  $\text{NH}_4\text{Cl}$ .

Cathode, reductions:  $2\text{MnO}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + 2\text{OH}^-(\text{aq})$

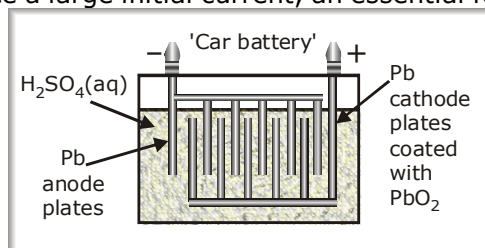
Anode, Oxidation:  $\text{Zn}(\text{s}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{ZnO}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^-$

Alkaline cells, which produce 1.54 V (approximately the same voltage as the LeClanche cell), have the further advantage that the cell potential does not decline under high current loads because no gases are formed.



### SECONDARY OR RECHARGEABLE BATTERIES

An automobile battery—the **lead storage battery** – is probably the best-known rechargeable battery figure. The 12-V version of this battery contains six voltaic cells, each generating about 2V. The lead storage battery can produce a large initial current, an essential feature when starting an automobile engine.



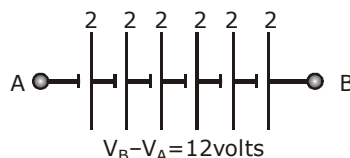
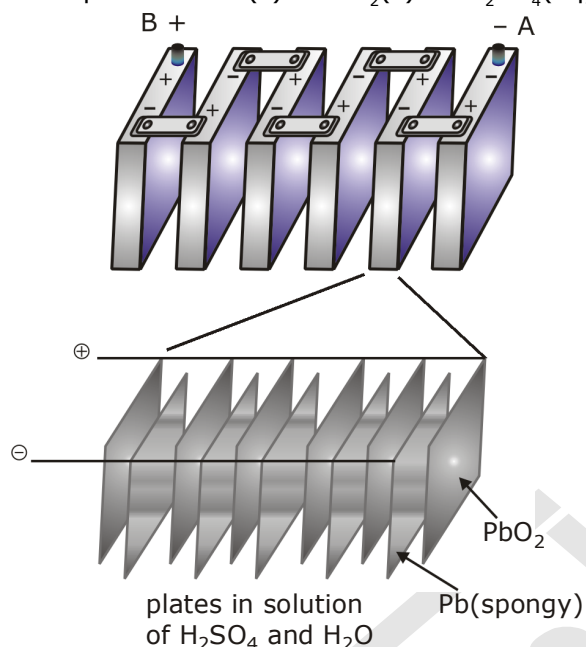
When the cell supplies electrical energy, the lead anode is oxidized to lead (II) sulfate, an insoluble

substance that adheres to the electrode surface. The two electrons produced per lead atom move through the external circuit to the cathode, where  $\text{PbO}_2$  is reduced to  $\text{Pb}^{2+}$  ions that in presence of  $\text{H}_2\text{SO}_4$ , also form lead (II) sulfate.

Cathode, reduction:  $\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\ell)$

Anode, oxidation:  $\text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$

Net ionic equation  $\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\ell)$



**A** The battery consists of six two-volt cells connected in series.

**B** Each component cell is composed of several negative and positive electrodes made of pure spongy lead and lead oxide, connected in parallel, are immersed in a dilute solution of sulfuric acid.

**Nickel-Cadmium ("Ni-Cad") batteries**, used in variety of cordless appliances such as telephones, video camcorders, and cordless power tools, are lightweight and rechargeable. The chemistry of the cell utilizes the oxidation of cadmium and the reduction of nickel (III) oxide under basic conditions. As with the lead storage battery, the reactants and products formed when producing a current are solids that adhere to the electrodes.

Cathode, reduction:  $\text{NiO}(\text{OH})(\text{s}) + \text{H}_2\text{O}(\ell) + \text{e}^- \rightarrow \text{Ni}(\text{OH})_2(\text{s}) + \text{OH}^-(\text{aq})$

Anode, Oxidation:  $\text{Cd}(\text{s}) + 2\text{OH}^- \rightarrow \text{Cd}(\text{OH})_2(\text{s}) + 2\text{e}^-$

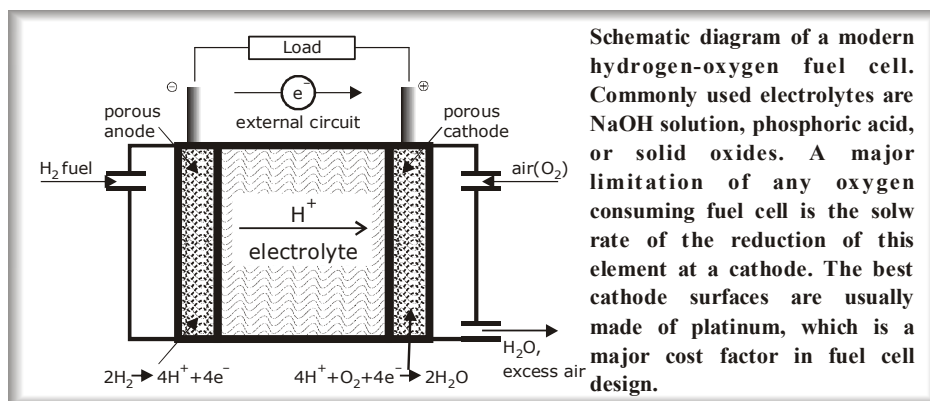
### **FUELCELLS AND HYBRID CARS**

An advantage of voltaic cells is that they are small and portable, but their size is also a limitation. The amount of electric current produced is limited by the quantity of reagents contained in the cell. When one of the reactants is completely consumed, the cell will no longer generate a current. Fuel cells avoid this limitation because the reactants (fuel and oxidant) can be supplied continuously to the cell from an external reservoir.

In a Hydrogen - Oxygen fuel cell figure, hydrogen is pumped onto the anode of the cell, and  $\text{O}_2$  (or air) is directed to the cathode where the following reactions occur.

Cathode, reduction:  $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\ell) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$   $E^\circ = 1.23 \text{ V}$

Anode, Oxidation:  $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$   $E^\circ = 0\text{V}$

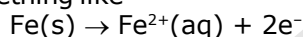


### CORROSION CELLS AND REACTIONS

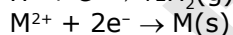
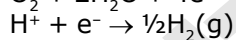
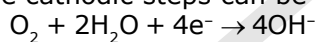
Corrosion can be defined as the deterioration of materials by chemical processes. Of these, the most important by far is electrochemical corrosion of metals, in which the oxidation process  $M \rightarrow M^+ + e^-$  is facilitated by the presence of a suitable electron acceptor, sometimes referred to in corrosion science as a **depolarizer**.

In a sense, corrosion can be viewed as the spontaneous return of metals to their ores: the huge quantities of energy that were consumed in mining, refining, and manufacturing metals into useful objects is dissipated by a variety of different routes.

The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive, so the electrons can flow through the metal from the anodic to the cathodic regions. The presence of water is necessary in order to transport ions to and from metal, but a thin film of adsorbed moisture can be sufficient. A corrosion system can be regarded as a short-circuited electrochemical cell in which the anodic process is something like



and the cathodic steps can be any of



where M is a metal. Which parts of the metal serve as anodes and cathodes can depend on many factors, as can be seen from the irregular corrosion patterns that are commonly observed. Atoms in regions that have undergone stress, as might be produced by forming or machining, often tend to have higher free energies, and thus tend to become anodic.

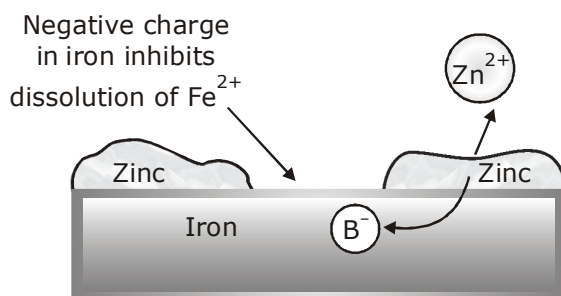
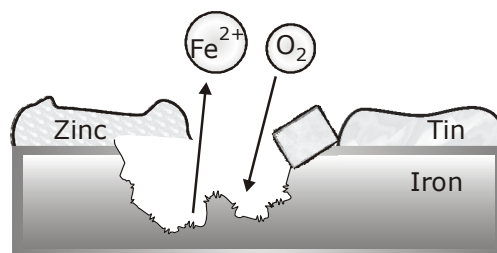
### CONTROL OF CORROSION

Since both the cathodic and anodic steps must take place for corrosion to occur, prevention of either one will stop corrosion. The most obvious strategy is to stop both processes by coating the object with a paint or other protective coating. Even if this is done, there are likely to be places where the coating is broken or does not penetrate, particularly if there are holes or screw threads.

A more sophisticated approach is to apply a slight negative charge to the metal, thus making it more difficult for the reaction  $M \rightarrow M^{2+} + 2e^-$  to take place.

### SACRIFICIAL COATINGS

One way of supplying this negative charge is to apply a coating of a more active metal. Thus a very common way of protecting steel from corrosion is to coat it with a thin layer of zinc; this process is known as galvanizing. The zinc coating, being less noble than iron, tends to corrode selectively. Dissolution of this sacrificial coating leaves behind electrons which concentrate in the iron, making it cathodic and thus inhibiting its dissolution.

**Sacrificial coating****Noble coating**

The effect of plating iron with a less active metal provides an interesting contrast. The common tin-plated can (on the right) is a good example. As long as the tin coating remains intact, all is well, but exposure of even a tiny part of the underlying iron to the moist atmosphere initiates corrosion. The electrons released from the iron flow into the tin, making the iron more anodic so now the tin is actively promoting corrosion of the iron! You have probably observed how tin cans disintegrate very rapidly when left outdoors.

### **CATHODIC PROTECTION**

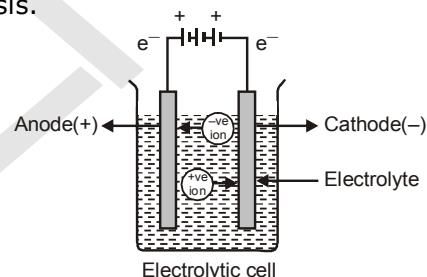
A more sophisticated strategy is to maintain a continual negative electrical charge on a metal, so that its dissolution as positive ions is inhibited. Since the entire surface is forced into the cathodic condition, this method is known as cathodic protection. The source of electrons can be an external direct current power supply (commonly used to protect oil pipelines and other buried structures), or it can be the corrosion of another, more active metal such as a piece of zinc or aluminum buried in the ground nearby.

### **ELECTROLYSIS**

The decomposition of electrolyte solution by passage of electric current, resulting into deposition of metals or liberation of gases at electrodes is known as electrolysis.

### **ELECTROLYTIC CELL**

This cell converts electrical energy into chemical energy. The entire assembly except that of the external battery is known as the electrolytic cell.

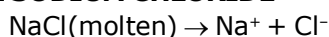


### **ELECTRODES**

The metal strip at which positive current enters is called **anode**; anode is positively charged in electrolytic cell. On the other hand, the electrode at which current leaves is called **cathode**. Cathodes are negatively charged.

Anode	Positive	Loss of electron or oxidation takes place	Positive Current enters
Cathode	Negative	Gain of electron or reduction takes place	Current leaves

### **ELECTROLYSIS OF MOLTEN SODIUM CHLORIDE**



Reactions at anode (oxidation) ; cathode (reduction)  
 $2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$  ;  $2\text{Na}^+ + 2\text{e}^- \rightarrow 2\text{Na}(\text{l})$

There are two types of electrodes used in the electrolytic cell, namely attackable and non-attackable. The attackable electrodes participate in the electrode reaction. They are made up of reactive metals

like Zn, Cu, Ag etc. In such electrodes, atom of the metal gets oxidised into the corresponding cation, which is passed into the solution. Thus, such anodes get dissolved and their mass decreases. On the other hand, non-attackable electrodes do not participate in the electrode reaction as they are made up of unreactive elements like Pt, graphite etc. Such electrodes do not dissolve and their mass remains the same.

### FARADAY'S LAWS OF ELECTROLYSIS :

#### (i) First law of electrolysis;

Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed (utilized) through the solution.

$$w \propto Q$$

$W$  = weight liberated,  $Q$  = charge in coulomb

$$w = ZQ$$

$Z$  = electrochemical equivalent

when  $Q = 1$  coulomb, then  $w = Z$

Thus, weight deposited by 1 coulomb charge is called electrochemical equivalent.

Let 1 ampere current is passed till ' $t$ ' seconds.

Then,  $Q = It$   $\therefore w = ZIt$

1 Faraday = 96500 coulomb = Charge of one mole electrons

**One faraday is the charge required to liberate or deposit one gm equivalent of a substance at corresponding electrode.**

Let ' $E$ ' is equivalent weight then ' $E$ ' gm will be liberated by 96500 coulomb.

$$\therefore 1 \text{ Coulomb will liberate } \frac{E}{96500} \text{ gm ; By definition, } Z = \frac{E}{96500}$$

$$\therefore W = \frac{ItE}{96500}$$

When a gas is evolved at an electrode, then above formula changes as,

$$V = \frac{ItV_e}{96500}$$

where  $V$  = volume of liberated gas,  $V_e$  = equivalent volume of gas.

Equivalent volume may be defined as:

The volume of gas liberated by 96500 coulomb at STP.

#### (ii) Second law of electrolysis :

When same amount of charge is passed through different electrolyte solutions connected in series then weight of substances deposited or dissolved at anode or cathode are in ratio of their equivalent weights. i.e.  $w_1/w_2 = E_1/E_2$

### QUALITATIVE ASPECTS OF ELECTROLYSIS

In the electrolysis process we have discussed above, we have taken molten salt as electrolyte, which contains only one cation and anion. Now, if the electrolyte taken contains more than one cation and anion (for example, aqueous solution of the ionic electrolyte), then the cation and anion that will get discharged depends on the ability of cation to get reduced and the ability of anion to get oxidised.

The ability of an ion to get oxidised or reduced depends upon the size, mass, positive charge, negative charge etc. Thus it is not possible to predict qualitatively that which ion would be discharged first, as one factor might enhance the ability to discharge while the other factor may hamper it. This can only be predicted on the basis of quantitative value assigned based on the cumulative effect of all the factors responsible for an ion's ability of discharge. The value is referred as standard potential, which is determined by keeping the concentration of ion as 1 M, pressure of gas at 1 atm, and the measurement done at 25°C. For a cation, the standard reduction potential (SRP) values are compared. The cation having higher standard reduction potential value is discharged in preference to cation with lower SRP value provided the ions are at 1M concentration. For an anion, the standard oxidation potential (SOP) values are compared and anion having higher SOP is preferentially discharged, if the concentration is 1

M for each of the ion. The SRP Values at 25° C for some of the reduction half reaction are given in the table below.

S. NO.	Reduction half cell reaction	E° involts at 25°C
1.	$F_2 + 2e^- \rightarrow 2F^-$	+ 2.65
2.	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	+ 2.01
3.	$Co^{3+} + e^- \rightarrow Co^{2+}$	+ 1.82
4.	$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	+ 1.65
5.	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+ 1.52
6.	$Au^{3+} + 3e^- \rightarrow Au$	+ 1.50
7.	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+ 1.36
8.	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+ 1.33
9.	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+ 1.229
10.	$Br_2 + 2e^- \rightarrow 2Br^-$	+ 1.07
11.	$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	+ 0.96
12.	$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	+ 0.92
13.	$Cu^{2+} + I^- + e^- \rightarrow CuI$	+ 0.86
14.	$Ag^+ + e^- \rightarrow Ag$	+ 0.799
15.	$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	+ 0.79
16.	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+ 0.77
17.	$I_2 + 2e^- \rightarrow 2I^-$	+ 0.535
18.	$Cu^+ + e^- \rightarrow Cu$	+ 0.53
19.	$Cu^{2+} + 2e^- \rightarrow Cu$	+ 0.34
20.	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	+ 0.27
21.	$AgCl + e^- \rightarrow Ag + Cl^-$	+ 0.222
22.	$Cu^{2+} + e^- \rightarrow Cu^+$	+ 0.15
23.	$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+ 0.13
24.	$2H^+ + 2e^- \rightarrow H_2$	+ 0.00

25.	$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	- 0.036
26.	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	- 0.126
27.	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	- 0.14
28.	$\text{AgI} + \text{e}^- \rightarrow \text{Ag} + \text{I}^-$	- 0.151
29.	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	- 0.25
30.	$\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}$	- 0.28
31.	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	- 0.403
32.	$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	- 0.41
33.	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	- 0.44
34.	$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	- 0.74
35.	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	- 0.762
36.	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	- 0.828
37.	$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	- 1.18
38.	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	- 1.66
39.	$\text{H}_2 + 2\text{e}^- \rightarrow 2\text{H}^-$	- 2.25
40.	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	- 2.37
41.	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	- 2.71
42.	$\text{Ca}^{2+} + \text{e}^- \rightarrow \text{Ca}$	- 2.87
43.	$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}$	- 2.90
44.	$\text{Cs}^+ + \text{e}^- \rightarrow \text{Cs}$	- 2.92
45.	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	- 2.93
46.	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	- 3.03

When solution of an electrolyte contains more than one type of cations and anions at concentrations different than 1 M, the discharge of an ion does not depend solely on standard potentials but also depends on the concentration of ion in the solution. The value is referred as potential, called as reduction potential for cation and oxidation potential for anion. The relation between reduction potential and standard reduction potential is given by Nernst equation, as

$$E_{RP} = E_{RP}^0 - \frac{RT}{nF} \ln \frac{[\text{concentration of product}]}{[\text{concentration of reactant}]}$$

Where  $E_{RP}$  = Reduction potential of cation and  $E_{RP}^0$  = Standard reduction potential of cation. Thus, it is possible that a cation ( $A^+$ ) with lower standard reduction potential getting discharged in preference to cation ( $B^+$ ) having higher standard reduction potential because their concentration might be such that the reduction potential of  $A^+$  is higher than that of  $B^+$ .

When two metal ions in the solution have identical values of their reduction potentials, the simultaneous deposition of both the metals will occur in the form of an alloy.

### CONDUCTANCE

#### Introduction:

Both metallic and electrolytic conductors obey Ohm's law

i.e.  $V = IR$

where  $V$  = Potential difference in volt;  $I$  Current in ampere ;  $R$  = resistance in Ohm

We know, resistance is directly proportional to length of conductor and inversely proportional to cross sectional area of the conductor.

$$R \propto \frac{\ell}{A} \text{ or } R = \rho \frac{\ell}{A} \quad (\rho = \text{specific resistance})$$

Specific resistance is the resistance of a conductor having lengths of 1 cm and cross sectional area of 1 cm<sup>2</sup>.

Unit of  $R$  is ohm and unit of specific resistance is ohm cm

**Reciprocal of resistance is called as conductance and reciprocal of specific resistance is called as specific conductance.**

$$\frac{1}{R} = \frac{1}{\rho} \frac{A}{\ell} \text{ or } C = K \frac{A}{\ell}$$

where  $C$  = conductance ohm<sup>-1</sup>;  $K$  = specific conductance ohm<sup>-1</sup> cm<sup>-1</sup>.

Mho and siemens are other units of conductance.

$$K = \frac{\ell}{A} C$$

Specific conductance = Cell constant x Conductance.

#### **SPECIFIC CONDUCTANCE IS CONDUCTANCE OF 1 CM<sup>3</sup> OF AN ELECTROLYTE SOLUTION.**

In case of electrolytic solution, the specific conductance is defined as the conductance of a solution of definite concentration enclosed in a cell having two electrodes of unit area separated by 1 cm apart.

#### 1. Equivalent Conductance

Equivalent conductance is the conductance of an electrolyte solution containing 1 gm equivalent of electrolyte. It is denoted by  $\wedge$ .

$$\wedge = K \times V$$

$$(\wedge = \text{ohm}^{-1} \text{ cm}^{-1} \times \text{cm}^3 = \text{ohm}^{-1} \text{ cm}^2)$$

Usually concentration of electrolyte solution is expressed as  $C$  gm equivalent per litre.

$$\text{Thus, } V = \frac{1000}{C}$$

$$\{\text{Volume having 1 gm equivalent electrolyte in the solution}\} \text{ Thus, } \wedge = K \times \frac{1000}{C}.$$

#### 2. Molar Conductance

Molar conductance may be defined as conductance of an electrolyte solution having 1 gm mole electrolyte in a litre. It is denoted by  $\wedge_m$ .

$$\wedge_m = K \times V$$

Usually concentration of electrolyte solution is expressed as ' $M$ ' gm mole electrolyte per litre.



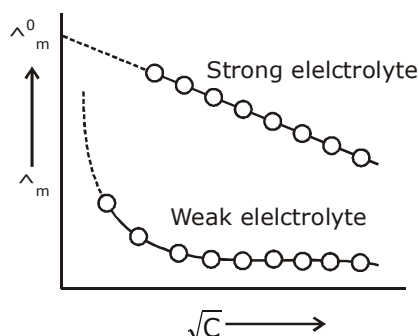
Thus, 
$$V = \frac{1000}{M}$$

Hence, 
$$\Lambda_m = K \times \frac{1000}{M}$$

**Relation between  $\Lambda_m$  and  $\Lambda_m^0$ :** 
$$\Lambda_m = n \times \Lambda_m^0$$

### DETERMINATION OF $\Lambda_m^0$ OR $\Lambda^0$

A plot of  $\Lambda_m$  vs  $\sqrt{C}$  as found experimentally is as shown below graphically.



the  $\Lambda_m$  vs  $\sqrt{C}$  plot of strong electrolyte being linear it can be extrapolated to zero concentration.

Thus,  $\Lambda_m$  values of the solution of the test electrolyte are determined at various concentrations the concentrations should be as low as good.

$\Lambda_m$  values are then plotted against  $\sqrt{C}$  when a straight line is obtained. This is the extrapolated to zero concentration. The point where the straight line intersects  $\Lambda_m$  axis is  $\Lambda_m^0$  of the strong electrolyte. However, the plot in the case weak electrolyte being non linear, shooting up suddenly at some low concentration and assuming the shape of a straight line parallel to  $\Lambda_m$  axis. Hence extrapolation in this case is not possible. Thus,  $\Lambda_m^0$  of a weak electrolyte cannot be determined experimentally. It can, however, be done with the help of Kohlrausch's law to be discussed later.

### Kohlrausch's Law of Independent Migration of Ions

Kohlrausch determine  $\Lambda_m^0$  values of pairs of some strong electrolytes containing same cation say KF and KCl, NaF and NaCl etc., and found that the difference in  $\Lambda_m^0$  value in each case remains the same

$$\Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{KF}) = \Lambda_m^0(\text{NaCl}) - \Lambda_m^0(\text{NaF})$$

He also determined  $\Lambda_m^0$  values of pairs of strong electrolytes containing same anion say KF and NaF, KCl and NaCl etc. and found that the difference in  $\Lambda_m^0$  values in each case remains the same.

$$\Lambda_m^0(\text{KF}) - \Lambda_m^0(\text{NaF}) = \Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{NaCl})$$

This experimental data led him to formulate the following law called Kohlrausch's law of independent migration of ions.

At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion which with it is associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions. Thus,

$$\Lambda_m^0 = \lambda_+^0 + \lambda_-^0$$

Where  $\lambda_+^0$  is the contribution of the cation  $\lambda_-^0$  is the contribution of the anion towards the molar conductance at infinite dilution. These contributions are called molar ionic conductances at infinite dilution. Thus,  $\lambda_+^0$  is the molar ionic conductance of cation and  $\lambda_-^0$  is the molar ionic conductance of anion, at infinite dilution. The above equation is, however, correct only for binary electrolyte like NaCl,  $\text{MgSO}_4$  etc.

### Application of Kohlrausch's law :

- (1) Determination of  $\Lambda_m^0$  of a weak electrolyte : In order to calculate  $\Lambda_m^0$  of a weak electrolyte say  $\text{CH}_3\text{COOH}$ , we determine experimentally  $\Lambda_m^0$  values of the following three strong electrolytes:

- (a) A strong electrolyte containing same cation as in the test electrolyte, say HCl  
 (b) A strong electrolyte containing same anion as in the test electrolyte, say CH<sub>3</sub>COONa  
 (c) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

$\Lambda_m^0$  of CH<sub>3</sub>COOH is the given as:

$$\Lambda_m^0(\text{CH}_3\text{COOH}) = \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{CH}_3\text{COONa}) - \Lambda_m^0(\text{NaCl})$$

Proof :

$$\Lambda_m^0(\text{HCl}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots\dots\dots(\text{i})$$

$$\Lambda_m^0(\text{CH}_3\text{COONa}) = \lambda_{\text{CH}_3\text{COO}^-}^0 + \lambda_{\text{Na}^+}^0 \quad \dots\dots\dots(\text{ii})$$

$$\Lambda_m^0(\text{NaCl}) = \lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots\dots\dots(\text{iii})$$

Adding equation (i) and equation (ii) and subtracting (iii) from them:

$$\Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{CH}_3\text{COONa}) - \Lambda_m^0(\text{NaCl}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{CH}_3\text{COO}^-}^0 = \Lambda_m^0(\text{CH}_3\text{COOH})$$

- (2) Determination of degree of dissociation ( $\alpha$ ) :

$$\alpha = \frac{\text{No. of molecules ionised}}{\text{total number of molecules dissolved}} = \frac{\Lambda_m}{\Lambda_m^0}$$

- (3) Determination of solubility of sparingly soluble salt

The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity water is deducted. The molar conductance of the saturated solution is taken to be equal to  $\Lambda_m^0$  as the saturated solution of a sparingly soluble salt is extremely dilute. Hence from equation (4).

$$\Lambda_m^0 = \frac{1000\kappa}{C}$$

Where C is the molarity of solution and hence the solubility.

**ATLAS**

## SOLVED EXAMPLE

**Ex.1** The reaction :  $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$  has a electrode potential of  $-0.76\text{ V}$ . This means-

- (A) Zn cannot replace hydrogen from acids (B) Zn is reducing agent  
(C) Zn is oxidizing agent (D)  $\text{Zn}^{2+}$  is a reducing agent

**Sol.** (B) Negative electrode potential shows that  $\text{Zn}^{2+}$  is difficult to be reduced and therefore, Zn acts as reducing agent.

**Ex.2** Certain quantity of current is passed through 2 voltmeters connected in series and containing  $\text{XSO}_4(\text{aq})$  and  $\text{Y}_2\text{SO}_4(\text{aq})$  respectively. If the atomic masses of X and Y are in the ratio of 2 : 1 the ratio of the masses of Y liberated to that of X is :

- (A) 1 : 1 (B) 1 : 2 (C) 2 : 1 (D) 3 : 2

**Sol.** (A)  $\text{X}^{2+} + 2\text{e}^- \rightarrow \text{X}$  ;  $\text{Y}^+ + \text{e}^- \rightarrow \text{Y}$

2 mol  $\text{e}^-$  produce X = 1 mol =  $1 \times \text{M g}$

2 mol  $\text{e}^-$  produce Y = 2 mol =  $2 \times \text{M}/2 = \text{M g}$

Hence, ratio of the masses of Y:X is M:M or 1:1

**Ex.3** The equivalent conductivities at infinite dilution of the cation and the anion of a salt  $\text{A}_2\text{B}$  are 140 and 80  $\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$  respectively. The equivalent conductivity of the salt at infinite dilution is-

- (A) 160  $\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$  (B) 220  $\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$   
(C) 60  $\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$  (D) 360  $\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$

**Sol.** (B)  $\Lambda_{\text{eq}}^\infty (\text{A}_2\text{B}) = \lambda_{\text{eq}}^\infty (\text{A}^+) + \lambda_{\text{eq}}^\infty (\text{B}^{2-})$

$$= 140 + 80 = 220 \text{ ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$$

**Ex.4** The specific conductance of a 0.20 mol  $\text{L}^{-1}$  solution of an electrolyte at  $20^\circ\text{C}$  is 2.48  $\times 10^{-4} \text{ ohm}^{-1} \text{cm}^{-1}$ . The molar conductivity of the solution is -

- (A) 1.24  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  (B) 4.96  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$   
(C) 1.24  $\text{ohm}^{-1} \text{cm}^2$  (D) 4.96  $\text{ohm}^{-1} \text{cm}^2$

**Sol.** (A)  $\Lambda_{\text{m}} = \frac{\kappa \times 1000}{M} = \frac{2.48 \times 10^{-4} \times 1000}{0.20}$

$$= 1.24 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$$

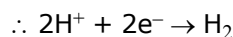
**Ex.5** When an electric current is passed through acidulated, water, 112 mL of hydrogen gas at N.T.P. collects at the cathode in 965 seconds. The current passed, in amperes, is-

- (A) 1.0 (B) 0.5 (C) 0.1 (D) 2.0

**Sol.** (A) 22,400 mL of hydrogen at STP(or NTP)=2g

$\therefore$  112 mL of hydrogen at

$$\text{STP} = \frac{2\text{g} \times 112\text{mL}}{22,400\text{mL}} = 10^{-2} \text{ g}$$



$$2\text{F} \quad 1 \text{ mol}$$

$$= 2 \times 96,500 \text{ C} = 2 \text{ g,}$$

$$2 \text{ g hydrogen is deposited by } 2 \times 96,500 \text{ C}$$

$$\therefore 10^{-2} \text{ g hydrogen will be deposited by } = \frac{2 \times 96,500 \times 10^{-2} \text{ g}}{2\text{g}} = 965 \text{ C}$$

$$Q = i \times t \quad 965 = i \times 965 \quad i = 1$$

- Ex.6** The charge required to deposit 40.5 g of Al (atomic mass = 27.0 g) from the fused  $\text{Al}_2(\text{SO}_4)_3$  is-  
 (A)  $4.34 \times 10^5 \text{ C}$  (B)  $43.4 \times 10^5 \text{ C}$  (C)  $1.44 \times 10^5$  (D) None of these

**Sol. (A)**  $\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$

$$3\text{F} \quad 1 \text{ mol} = 27.0 \text{ g}$$

to deposit 27g required charge =  $3 \times 96,500 \text{ C}$

$\therefore$  to deposit 40.4g required charge

$$= \frac{40.5\text{g} \times 3\text{mol} \times 96,500\text{C mol}^{-1}}{27.0\text{g}} = 4.34 \times 10^5 \text{ C}$$

- Ex.7** The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate and chromium nitrate respectively. If 0.3 g of nickel was deposited in the first cell, the amount of chromium deposited is (At. wt. Ni= 59, Cr=52)  
 (A) 0.1 g (B) 0.176 g (C) 0.3 g (D) 0.6 g

**Sol. (B)**  $\frac{m_{\text{Ni}}}{m_{\text{Cr}}} = \frac{\text{Eq. mass of Ni}}{\text{Eq. mass of Cr}}$

For  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$ , we have :

$$\frac{0.3 \text{ g}}{m_{\text{Cr}}} = \frac{59/2}{52/3} \quad m_{\text{Cr}} = \frac{0.3\text{g} \times \frac{52}{3}}{(59/2)} = 0.176 \text{ g}$$

- Ex.8** Electrolytic conduction differs from metallic conduction. In case of metallic conduction -  
 (A) The resistance increases with increasing temperature  
 (B) The resistance decreases with increasing temperature  
 (C) The flow of current does not generate heat  
 (D) The resistance is independent of the length of electrolytic conductor

**Sol. (A)** With increase in temperature vibration of Kernal (Cation) increases and therefore, conduction decreases and hence, resistance of the metallic conductor increases.

- Ex.9** Three faraday of electricity is passed through molten solutions of  $\text{AgNO}_3$ ,  $\text{NiSO}_4$  and  $\text{CrCl}_3$  kept in three vessels using inert electrodes. The ratio in mol in which the metals Ag, Ni and Cr will be deposited is-  
 (A) 1 : 2 : 3 (B) 3 : 2 : 1 (C) 6 : 3 : 2 (D) 2 : 3 : 6

**Sol. (C)** (i)  $\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$

$$\begin{array}{ll} 1 \text{ mol} = 1\text{F} & 1 \text{ mol} \\ 3 \text{ F} & 3 \text{ mol} \end{array}$$

(ii)  $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ni}(\text{s})$

$$\begin{array}{ll} 2 \text{ mol} = 2 \text{ F} & 1 \text{ mol} \\ 3 \text{ F} & 3/2 \text{ mol} \end{array}$$

(iii)  $\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Cr}(\text{s})$

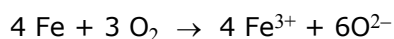
$$3 \text{ mol} = 3 \text{ F} \quad 1 \text{ mol}$$

The required ratio of moles of Ag, Ni and Cr is :

$$3 \text{ mol Ag} : 3/2 \text{ mol Ni} : 1 \text{ mol Cr}$$

or **6 mol Ag : 3 mol Ni : 2 mol Cr.**

**Ex.10** In the reaction :



which of the following statements is correct

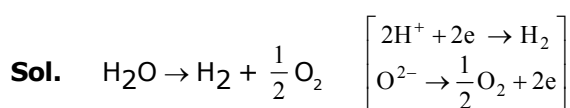
- (A) A redox reaction (B)  $\text{O}_2$  is reducing agent  
(C)  $\text{Fe}^{3+}$  is an oxidizing agent (D) Fe is reduced to  $\text{Fe}^{3+}$

**Sol.** (A) In this reaction, Fe is oxidized to  $\text{Fe}^{3+}$  and  $\text{O}_2$  is reduced to  $\text{O}^{2-}$ .

**Ex.11** Calculate current strength in ampere required to deposit 10 g Zn in 2hrs. At wt. of Zn = 65.

**Sol.**  $\therefore w = \frac{\text{E.i.t.}}{96500}$  ;  $\therefore i = \frac{96500 \times w}{\text{E.t.}}$   $\left[ \begin{array}{l} \because \text{Zn}^{2+} + 2\text{e} \rightarrow \text{Zn} \\ \therefore E = \frac{\text{At. wt.}}{2} = \frac{65}{2} \end{array} \right]$   $i = \frac{96500 \times 10 \times 2}{65 \times 2 \times 60 \times 60} = 4.12 \text{ ampere}$

**Ex.12** How many hour are required for a current of 3.0 ampere to decompose 18 g water.



$$\therefore \text{Eq. of H}_2\text{O} = \frac{\text{i.t.}}{96500}$$

Equivalent weight of  $\text{H}_2\text{O} = 18/2$  as two electrons are used for 1 mole  $\text{H}_2\text{O}$  to decompose in  $\text{H}_2$  and  $\text{O}_2$ .

$$\therefore \frac{18}{18/2} = \frac{3 \times t}{96500}$$

$$\therefore t = 64333.3 \text{ sec} = 1072.2 \text{ minute} = 17.87 \text{ hr}$$

**Ex.13** Calculate the Avogadro's number using the charge on the electron  $1.60 \times 10^{-19} \text{ C}$  and the fact that 96500 C deposits 107.9 g silver from its solution.

**Sol.**  $\therefore$  96500 coulomb deposits 107.9 g Ag

Here eq. wt = Atomic weight

because Ag is monovalent. Thus 96500 coulomb charge means charge on N electrons where N in Av. no.

$$\text{Thus } N \times e = 96500$$

$$N = \frac{96500}{1.60 \times 10^{-19}}$$

$$= 6.03 \times 10^{23} \text{ electrons}$$

**Ex.14** Calculate the volume of gases liberated at anode and cathode at NTP from the electrolysis of  $\text{Na}_2\text{SO}_4(\text{aq.})$  solution by a current of 2 ampere passed for 10 minute.

**Sol.** At cathode :  $2\text{H}_2\text{O} + 2\text{e} \rightarrow \text{H}_2 + 2\text{OH}^-$

At anode :  $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4\text{e} + \text{O}_2$

$$\therefore \text{At anode } E_{\text{O}_2} = \frac{32}{4} = 8 \quad \therefore w_{\text{O}_2} = \frac{\text{E.i.t.}}{96500} = \frac{32 \times 2 \times 10 \times 60}{4 \times 96500} = 0.0995 \text{ g}$$

$$\text{At NTP : Volume of O}_2 = \frac{0.0995 \times 22.4}{32} = 0.0696 \text{ litre}$$

$$\text{Similarly at cathode } w_{\text{H}_2} = \frac{\text{E.i.t.}}{96500} = \frac{2 \times 2 \times 10 \times 60}{2 \times 96500} = 0.0124 \text{ g}$$

$$\text{At NTP : Volume of H}_2 = \frac{0.0124 \times 22.4}{2} = 0.139 \text{ litre}$$

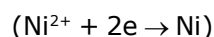
**Ex.15** Fused  $\text{Ni}(\text{NO}_3)_2$  is electrolysed between platinum electrodes using a current of 5 ampere for 20 minute. What mass of Ni is deposited at the cathode ?

**Sol.** Eq. of Ni deposited

$$\frac{w}{E} = \frac{i \cdot t}{96500} = \frac{5 \times 20 \times 60}{96500}$$

$$= 0.0622$$

$$\text{or } w_{\text{Ni}} = 0.0622 \times 58.71/2 = 1.825 \text{ g}$$



**Ex.16** A current of 3.7 ampere is passed for 6 hrs. between Ni electrodes in 0.5 litre of 2M solution of  $\text{Ni}(\text{NO}_3)_2$ . What will be the molarity of solution at the end of electrolysis ?

**Sol.** The electrolysis of  $\text{Ni}(\text{NO}_3)_2$  in presence of Ni electrode will bring in following changes :



Thus, there will be no change in conc. of  $\text{Ni}(\text{NO}_3)_2$  solution during electrolysis i.e. ,

It will remain 2M

**Ex.17** How long a current of 3 ampere has to be passed through a solution of  $\text{AgNO}_3$  to coat a metal surface of  $80 \text{ cm}^2$  with a thickness of  $0.005 \text{ mm}$  ? Density of Ag is  $10.5 \text{ g cm}^{-3}$

**Sol.** Given ,  $i = 3$  ampere

Also Volume covered by

$$\text{Ag} = 80 \times 0.005 \times 10^{-1} \text{ cm}^3 = 0.04 \text{ cm}^3$$

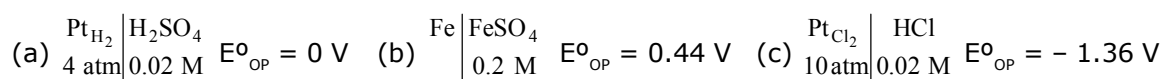
$$\therefore \text{Weight of Ag used} = 0.04 \times 10.5 \text{ g}$$

$$w_{\text{Ag}} = \frac{\text{E.i.t.}}{96500}$$

$$0.04 \times 10.5 = \frac{108 \times 3 \times t}{96500}$$

$$\therefore t = 125.09 \text{ sec.}$$

**Ex.18** Calculate e.m.f of half cells given below :



**Sol.** (a)  $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$

$$\therefore E_{\text{OP}} = E_{\text{OP}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2}} \quad [\text{H}^+ = 0.02 \times 2\text{M}]$$

$$= 0 - \frac{0.059}{2} \log \frac{(0.02 \times 2)^2}{4} \quad E_{\text{OP}_{\text{H}_2/\text{H}^+}} = + 0.100 \text{ V}$$

(b)  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$   $\therefore E_{\text{OP}} = E_{\text{OP}}^{\circ} - \frac{0.059}{2} \log [\text{Fe}^{2+}]$

$$= 0.44 - \frac{0.059}{2} \log [0.2] \quad E_{\text{OP}_{\text{Fe}/\text{Fe}^{2+}}} = + 0.4606 \text{ volt.}$$

(c)  $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$   $\therefore E_{\text{OP}} = E_{\text{OP}}^{\circ} - \frac{0.059}{2} \log \frac{P_{\text{Cl}_2}}{[\text{Cl}^-]^2}$

$$= -1.36 - \frac{0.059}{2} \log \frac{10}{(0.02)^2} \quad E_{\text{OP}_{\text{Cl}^-/\text{Cl}_2}} = - 1.49 \text{ volt}$$

**Ex.19** If the oxidation of oxalic acid by acidified  $\text{MnO}_4^-$  solution were carried out in a reversible cell, what would be the electrode reaction? Also calculate the equilibrium constant of the reaction. Given

$$E_{\text{Mn}^{7+}/\text{Mn}^{2+}}^{\circ} = + 1.51 \text{ V and } E_{\text{CO}_2/\text{C}_2\text{O}_4^{2-}}^{\circ} = - 0.49 \text{ V.}$$

**Sol.**  $E_{\text{RP Mn}^{7+}/\text{Mn}^{2+}}^{\circ} = + 1.51 \text{ V}$   $\therefore E_{\text{OP Mn}^{2+}/\text{Mn}^{7+}}^{\circ} = - 1.51 \text{ V}$

$$E_{\text{RP CO}_2/\text{C}_2\text{O}_4^{2-}}^{\circ} = - 0.49 \text{ V} \quad E_{\text{OP C}_2\text{O}_4^{2-}/\text{CO}_2}^{\circ} = + 0.49 \text{ V}$$

More is  $E_{\text{OP}}$ , more is the tendency to get oxidise



$$\therefore E_{\text{Cell}}^{\circ} = E_{\text{OP}}^{\circ} + E_{\text{RP}}^{\circ} = 0.49 + 1.51 = 2.0 \text{ V} \quad \text{Also } E^{\circ} = \frac{0.059}{n} \log K_{\text{C}}$$

$$\therefore 2 = \frac{0.059}{10} \log K_{\text{C}} \quad \therefore K_{\text{C}} = 10^{338.98}$$

**Ex.20** The e.m.f. of cell,

$\text{Ag}|\text{AgI}_{(\text{s})}, 0.05 \text{ MKI} || 0.05 \text{ M AgNO}_3 | \text{Ag}$ , is 0.788 V. Calculate solubility product of AgI.

**Sol.**  $K_{\text{sp}}$  of AgI =  $[\text{Ag}^+][\text{I}^-] = [\text{Ag}^+][0.05]$

For given cell  $E_{\text{Cell}} = E_{\text{OPAg}} + E_{\text{RPAg}} \quad \dots(i)$

$$= E_{\text{OPAg}/\text{Ag}^+} - \frac{0.059}{1} \log [\text{Ag}^+]_{\text{L.H.S.}} + E_{\text{RPAg}^+/\text{Ag}} + \frac{0.059}{1} \log [\text{Ag}^+]_{\text{R.H.S.}} \quad E_{\text{Cell}} = \frac{0.059}{1} \log \frac{[\text{Ag}^+]_{\text{R.H.S.}}}{[\text{Ag}^+]_{\text{L.H.S.}}}$$

$$\left[ \because E_{\text{OP Ag}^+/\text{Ag}}^{\circ} = E_{\text{RP Ag}^+/\text{Ag}}^{\circ} \right] \quad 0.788 = \log \frac{0.05}{[\text{Ag}^+]_{\text{L.H.S.}}} \quad \therefore [\text{Ag}^+]_{\text{L.H.S.}} = 2.203 \times 10^{-15}$$

$$\text{By equation (i)} \quad K_{\text{sp}} = [2.203 \times 10^{-15}] [0.05]$$

$$K_{\text{sp AgI}} = 1.10 \times 10^{-16}$$

**Ex.21** Calculate the reduction potential of a half cell consisting of a platinum electrode immersed in 2.0 M  $\text{Fe}^{2+}$  and 0.02 M  $\text{Fe}^{3+}$  solution. Given  $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = 0.771 \text{ V}$ .

**Sol.** The half cell reaction is :  $\text{Fe}^{3+} + e \longrightarrow \text{Fe}^{2+}$  (or take  $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e$ )

$$\text{Thus } E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} + \frac{0.059}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

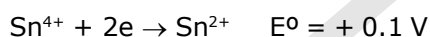
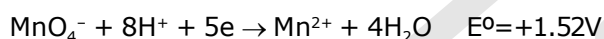
$$\therefore E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.771 + \frac{0.059}{1} \log \frac{0.02}{2.0} = 0.771 + \frac{0.059}{1} \log 10^{-2} = 0.653 \text{ V}$$

**Ex.22** An electrochemical cell has two half cell reactions as,  $\text{A}^{2+} + 2e^- \longrightarrow \text{A}$ ;  $E^{\circ} = 0.34 \text{ V}$ ,  $\text{X} \longrightarrow \text{X}^{2+} + 2e^-$ ;  $E^{\circ} = +2.37 \text{ V}$ . The cell voltage will be

- (A) 2.71 V                      (B) 2.03 V                      (C) - 2.71 V                      (D) - 2.03 V

**Sol.** (A)  $E_{\text{cell}} = 0.34 + 2.37 = 2.71 \text{ V}$

**Ex.23**  $E^{\circ}$  of some oxidants are given as :



(a) Select the strongest reductant and oxidant in these.

(b) Select the weakest reductant and oxidant in these.

(c) Select the spontaneous reaction from the changes given below :



**Sol.** (a) More or +ve the  $E_{\text{OP}}$ , more is the tendency for oxidation or stronger is reductant. Therefore, since maximum  $E_{\text{OP}}$  stands for

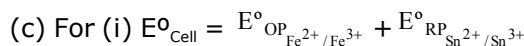


$\therefore$  strongest reductant :  $\text{Sn}^{2+}$ , and weakest oxidant :  $\text{Sn}^{4+}$

(b) More or +ve is  $E_{\text{RP}}$ , more is the tendency for reduction or stronger is oxidant. Therefore, since maximum  $E_{\text{RP}}$  stands for :  $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ ,  $E_{\text{RP}}^{\circ} = +1.52 \text{ V}$

$\therefore$  strongest oxidant :  $\text{MnO}_4^-$ , and weakest reductant:  $\text{Mn}^{2+}$

Note : Stronger is oxidant, weaker is its conjugate reductant and vice-versa.



$$= -0.77 + 0.1$$

$\therefore \text{Fe}^{2+}$  oxidizes and  $\text{Sn}^{4+}$  reduces in change,  $E_{\text{Cell}}^{\circ} = -0.67 \text{ V}$ ,  $E_{\text{Cell}}^{\circ}$  is negative

$\therefore$  (i) Is non-spontaneous change



$$\text{For (ii) } E^\circ_{\text{Cell}} = E^\circ_{\text{OP}_{\text{Fe}^{2+}/\text{Fe}^{3+}}} + E^\circ_{\text{RP}_{\text{I}_2/\text{I}^-}} = -0.77 + 0.54 = -0.23 \text{ V}$$

$\therefore$  (ii) Is non-spontaneous change

$$\text{For (iii) } E^\circ_{\text{Cell}} = E^\circ_{\text{OP}_{\text{I}_2/\text{I}^-}} + E^\circ_{\text{RP}_{\text{Sn}^{4+}/\text{Sn}^{2+}}} = -0.54 + 0.1 = -0.44 \text{ V}$$

$\therefore$  (iii) Is non-spontaneous change

$$\text{For (iv) } E^\circ_{\text{Cell}} = E^\circ_{\text{OP}_{\text{Sn}^{4+}/\text{Sn}^{2+}}} + E^\circ_{\text{RP}_{\text{I}_2/\text{I}^-}} = -0.1 + 0.54 = +0.44 \text{ V}$$

(iv) Is spontaneous change

**Ex.24** Calculate the standard cell potentials of galvanic cell in which the following reactions take place : (Given  $E^\circ_{\text{OP}}$  Cr, Cd,  $\text{Fe}^{2+}$ , Ag are 0.74V, 0.40 V, -0.77 V and -0.80 V respectively)



Calculate the  $\Delta_r G^\circ$  and equilibrium constant of the reactions.

**Sol.** (a)  $E^\circ_{\text{Cell}} = E^\circ_{\text{OP}_{\text{Cr}/\text{Cr}^{3+}}} + E^\circ_{\text{RP}_{\text{Cd}^{2+}/\text{Cd}}}$

$$[2\text{Cr} \rightarrow 2\text{Cr}^{3+} + 6\text{e}; 3\text{Cd}^{2+} + 6\text{e} \rightarrow 3\text{Cd}]$$

$$= 0.74 + (-0.40) = +0.34 \text{ V}$$

Six electrons ( $n = 6$ ) are used in redox change

$$-\Delta_r G^\circ = nE^\circ F = 6 \times 0.34 \times 96500 \text{ J} = 196860 \text{ J}$$

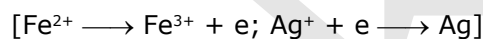
$$\text{or } \Delta_r G^\circ = -196.86 \text{ kJ}$$

$$\text{Also } -\Delta_r G^\circ = 2.303 RT \log K$$

$$\therefore 196860 = 2.303 \times 8.314 \times 298 \log K$$

$$K = 3.17 \times 10^{34}$$

(b)  $E^\circ_{\text{Cell}} = E^\circ_{\text{OP}_{\text{Fe}^{2+}/\text{Fe}^{3+}}} + E^\circ_{\text{RP}_{\text{Ag}^+/\text{Ag}}}$



$$= -0.77 + 0.80 = 0.03 \text{ V}$$

$$\text{Also } -\Delta_r G^\circ = nE^\circ F = 1 \times 0.03 \times 96500$$

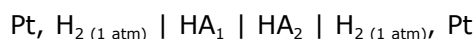
$$\text{or } \Delta_r G^\circ = -2895 \text{ J}$$

$$\text{Also } -\Delta_r G^\circ = 2.303 RT \log K$$

$$2895 = 2.303 \times 8.314 \times 298 \log K$$

$$K = 3.22$$

**Ex.25** A cell is constituted as follows



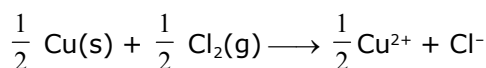
The pH of two acids solutions  $\text{HA}_1$  and  $\text{HA}_2$  are 5 and 3 respectively. The emf of the cell is

(A) 0.059 V (B) 0.0295 V (C) 0.118 V (D) -0.118 V

**Sol.** (C)  $\text{pH}_1 = 3 \therefore [\text{H}^+]_c = 1 \times 10^{-3} \text{ M}; \text{pH}_2 = 5 \therefore [\text{H}^+]_a = 1 \times 10^{-5}$

$$\text{Now, } E_{\text{cell}} = \frac{0.059}{1} \log \frac{[1 \times 10^{-3}]}{[1 \times 10^{-5}]} = 0.059 \times 2 = 0.118 \text{ V}$$

**Ex.26** The standard EMF of the cell reaction



is 1.02 V. The value of  $\Delta G^\circ$  will be

- (A) unpredictable (B) – 98.43 kJ (C) – 196.86 kJ (D) – 98.43 J

**Sol.** (B)  $\Delta G^\circ = -nFE^\circ = -1 \times 96500 \times 1.02$   
 $= -98430 \text{ J}$   
 or  $= -98.43 \text{ kJ}$

**Ex.27** A current of 1.70 ampere is passed through 300 mL of 0.160 M solution of  $\text{ZnSO}_4$  for 230 sec with a current efficiency of 90%. Find the molarity of  $\text{Zn}^{2+}$  after the deposition of Zn. Assume the volume of the solution remains constant during electrolysis.

**Sol.** We know,  $i = \frac{1.70 \times 90}{100}$  ampere

$$\therefore \text{Eq. of } \text{Zn}^{2+} \text{ lost} = \frac{i \cdot t}{96500} = \frac{1.70 \times 90 \times 230}{100 \times 96500} = 3.646 \times 10^{-3}$$

$$\therefore \text{Meq. of } \text{Zn}^{2+} \text{ lost} = 3.646$$

$$\text{Initial Meq. of } \text{Zn}^{2+} = 300 \times 0.160 \times 2$$

$$[\because M \times 2 = N \text{ for } \text{Zn}^{2+}, \text{Meq.} = N \times V_{(\text{in mL})}] = 48 \times 2 = 96$$

$$\therefore \text{Meq. of } \text{Zn}^{2+} \text{ left in solution} = 96 - 3.646 = 92.354$$

$$\therefore [\text{ZnSO}_4] = \frac{92.354}{2 \times 300} = 0.154 \text{ M}$$

**Ex.28** If 0.01 M solution of an electrolyte has a resistance of 40 ohms in a cell having a cell constant of 0.4  $\text{cm}^{-1}$  then its molar conductance in  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  will be :

- (A)  $10^4$  (B)  $10^3$  (C)  $10^2$  (D) 10

**Sol.** (B)  $K = \frac{1}{R} \times \text{cell const.} = \frac{0.4}{40} = 10^{-2}$

$$L_m = \frac{K \times 1000}{\text{Molarity}} = \frac{10^{-2} \times 1000}{10^{-2}} = 1000 = 10^3 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$$

**Ex.29** Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if current efficiency is 50%. If the potential drops across the cell is 3.0 volt, how much energy will be consumed ?

**Sol.**  $\text{C}_6\text{H}_5\text{NO}_2 + 6\text{H}^+ + 6\text{e} \longrightarrow \text{C}_6\text{H}_5\text{NH}_2 + 2\text{H}_2\text{O}$   
 $\text{N}^{3+} + 6\text{e} \longrightarrow \text{N}^{3-}$

$$\therefore \text{Eq. wt. of nitrobenzene} = \frac{M}{6} = \frac{123}{6}, \quad \text{Since current efficiency is 50\%} \quad \therefore i = \frac{50i_0}{100}$$

$$\text{Now } w = \frac{E \cdot i \cdot t}{96500} \quad 12.3 = \frac{123 \times i \times t \times 50}{6 \times 100 \times 96500} \quad \therefore i \times t = 115800 \text{ coulomb}$$

$$\text{Now energy used} = Q \times V = 115800 \times 3 = 347.4 \text{ kJ}$$

**Ex.30** A cell is containing two H electrodes. The negative electrode is in contact with a solution of  $10^{-6}$  M  $H^+$  ion. The e.m.f. of the cell is 0.118 volt at  $25^\circ\text{C}$ . Calculate  $[H^+]$  at positive electrode.

**Sol. Anode :**  $H_2 \longrightarrow 2H^+ + 2e$

(negative polarity)  $[H^+] = 10^{-6}$  M

**Cathode :**  $2H^+ + 2e \longrightarrow H_2$

(positive polarity).  $[H^+] \longrightarrow aM$

$$\therefore E_{\text{cell}} = E_{\text{OP}_{H/H^+}} + E_{\text{RP}_{H^+/H}} = E_{\text{OP}_{H/H^+}} - \frac{0.059}{2} \log_{10} [H^+]^2_{\text{Anode}} + E_{\text{RP}_{H^+/H}} + \frac{0.059}{2} \log_{10} [H^+]^2_{\text{Cathode}}$$

$$= \frac{0.059}{2} \log_{10} \frac{[H^+]^2_{\text{Cathode}}}{[H^+]^2_{\text{Anode}}}, \quad 0.118 = \frac{0.059}{2} \log_{10} \frac{[H^+]^2_{\text{Cathode}}}{(10^{-6})^2} = \frac{0.059}{1} \log_{10} \frac{[H^+]_{\text{Cathode}}}{10^{-6}}, \therefore [H^+]_{\text{Cathode}} = 10^{-4} \text{ M}$$

**Ex.31** A current of 2.0 A passed for 5 hours through a molten metal salt deposits 22.2 g of metal (At wt. = 177). The oxidation state of the metal in the metal salt is :

(A) + 1

(B) + 2

(C) + 3

(D) + 4

**Sol. (C)**  $E = \frac{m}{Q} \times 96500 = \frac{22.2}{2 \times 5 \times 60 \times 60} \times 96500 = 59.5$

$$\text{Oxi. state} = \frac{\text{At. wt.}}{\text{Eq. wt.}} = \frac{177}{59.5} = 3$$

**Ex.32** Cost of electricity for the production of x L  $H_2$  at NTP at cathode is Rs x; then cost of production of x L  $O_2$  at NTP at anode will be (assume 1 mole of electron as one unit of electricity)

(A) 2x

(B) 4x

(C) 16x

(D) 32x

**Sol. (A)**

$$\frac{\text{Volume of } H_2}{\text{Volume of } O_2} = \frac{\text{Equivalent volume of } H_2}{\text{Equivalent volume of } O_2}, \quad \frac{x}{\text{Volume of } O_2} = \frac{11.2}{5.6} = 2, \quad \text{Volume of } O_2 = \frac{x}{2}$$

Thus,  $\frac{x}{2}$  L  $O_2$  requires Rs x for its production. i.e., x L  $O_2$  will require Rs x for its production.

**Ex.33** In which direction can the reaction,  $2Hg(l) + 2Ag^+(aq.) \rightleftharpoons 2Ag(s) + Hg_2^{2+}(aq.)$  proceed spontaneously at the following concentrations of the ions participating in the reactions (i) and (ii) ?

(i)  $[Ag^+] = 10^{-4} \text{ mol L}^{-1}$  and  $[Hg_2^{2+}] = 10^{-1} \text{ mol L}^{-1}$

(ii)  $[Ag^+] = 10^{-1} \text{ mol L}^{-1}$  and  $[Hg_2^{2+}] = 10^{-4} \text{ mol L}^{-1}$

Given :  $E^\circ_{Hg_2^{2+}/Hg} = 0.79 \text{ V}$ ;  $E^\circ_{Ag^+/Ag} = 0.80 \text{ V}$

**Sol. (i)**  $Q = \frac{[Hg_2^{2+}]}{[Ag^+]^2} = \frac{10^{-1}}{[10^{-4}]^2} = 10^7$ ,  $E^\circ = E^\circ_{Ag^+/Ag} - E^\circ_{Hg_2^{2+}/Hg} = 0.80 - 0.79 = 0.01 \text{ V}$

$$E = E^{\circ} - \frac{0.059}{n} \log Q = 0.01 - \frac{0.059}{2} \log 10^7 = -0.1965 \text{ V}$$

Negative value shows that the reaction will proceed from right to left, i.e. in backward direction.

$$\begin{aligned} \text{(ii) } Q &= \frac{[\text{Hg}_2^{2+}]}{[\text{Ag}^+]^2} = \frac{10^{-4}}{[10^{-1}]^2} = 10^{-2}, E^{\circ} = 0.01 \text{ volt}, E = E^{\circ} - \frac{0.059}{n} \log_{10} Q = 0.01 - \frac{0.059}{2} \log_{10} 10^{-2} \\ &= 0.01 + 0.059 \text{ V} = 0.069 \text{ V} \end{aligned}$$

Since, the value of cell potential is positive, the reaction will proceed spontaneously in forward direction.

**Ex.34** Two students use same stock solution of  $\text{ZnSO}_4$  and a solutions of  $\text{CuSO}_4$ . The e.m.f. of one cell is 0.03 V higher than the other. The conc. of  $\text{CuSO}_4$  in the cell with higher e.m.f. value is 0.5 M. Find out the conc. of  $\text{CuSO}_4$  in the other cell  $[(2.303 RT/F) = 0.06]$ .

**Sol.** As given,

$$\text{Cell I : } \text{Zn} \left| \text{ZnSO}_4 \right|_{C_1} \left| \text{CuSO}_4 \right|_{C_2} \text{Cu}, \quad E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.06}{2} \log \frac{C_2}{C_1} \dots \text{(i)}$$

$$\text{Cell II : } \text{Zn} \left| \text{ZnSO}_4 \right|_{C_1} \left| \text{CuSO}_4 \right|_{C_2} \text{Cu}, \quad E'_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.06}{2} \log \frac{C_2}{C_1} \dots \text{(ii)}$$

If  $E_{\text{cell}} > E'_{\text{cell}}$ , then  $E_{\text{cell}} - E'_{\text{cell}} = 0.03 \text{ V}$  and  $C_2 = 0.5 \text{ M}$

By Eq. (i) and (ii)

$$E_{\text{cell}} - E'_{\text{cell}} = \frac{0.06}{2} \log \frac{C_2}{C'_2}, \quad 0.03 = \frac{0.06}{2} \log \frac{0.5}{C'_2}, \quad C'_2 = 0.05 \text{ M}$$

**Ex.35** How much will the reduction potential of a hydrogen electrode change when its solution initially pH = 0 is neutralized to pH = 7.

(A) Increase by 0.059 V (B) Decrease by 0.058 V (C) Increase by 0.41 V (D) Decrease by 0.41 V

**Sol.** (D)  $E^{\circ} = E + \frac{0.059}{1} \log 10^{-7} = E^{\circ} + \frac{0.059 \times (-7)}{1} = E^{\circ} - 0.41 \text{ V}$

**Ex.36** The time required to coat a metal surface of  $80 \text{ cm}^2$  with  $5 \times 10^{-3} \text{ cm}$  thick layer of silver (density  $1.05 \text{ g cm}^{-3}$ ) with the passage of 3A current through a silver nitrate solution is.

(A) 115 sec (B) 125 sec (C) 135 sec (D) 145 sec

**Sol.** (B) Weight of Ag required

$$= 80 \times 5 \times 10^{-3} \times 1.05 \text{ (wt. = V} \times \text{d)} = 0.42 \text{ g}$$

$$\therefore w = \frac{E \cdot i \cdot t}{96500} \quad \therefore 0.42 = \frac{108 \times 3 \times t}{96500} \quad \therefore t = 125 \text{ sec}$$

**Ex.37** Standard electrode potentials are

$\text{Fe}^{2+}/\text{Fe}$  ( $E^{\circ} = -0.44 \text{ V}$ ),  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ( $E^{\circ} = 0.77 \text{ V}$ )

$\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and Fe blocks are kept together, then :

(A)  $\text{Fe}^{3+}$  increases (B)  $\text{Fe}^{3+}$  decreases  
(C)  $\text{Fe}^{2+}/\text{Fe}^{3+}$  remains unchanged (D)  $\text{Fe}^{2+}$  decreases

**Sol. (B)**  $\text{Fe}^{+2} \longrightarrow \text{Fe} + \text{Fe}^{+3}$ ,  $E_{\text{cell}}^{\circ} = E_{\text{C}}^{\circ} - E_{\text{A}}^{\circ} = -0.44 - 0.77 = \ominus$

So spontaneous reaction is  $\text{Fe} + \text{Fe}^{+3} \rightarrow \text{Fe}^{+2}$

**Ex.38** Conductivity (Unit : siemen's S) is directly proportionally to the area of the vessel and the concentration of the solution in it and is inversely proportional to the length of vessel, then the unit of constant of proportionality is

- (A)  $\text{S m mol}^{-1}$  (B)  $\text{S m}^2 \text{mol}^{-1}$  (C)  $\text{S}^{-2} \text{m}^2 \text{mol}$  (D)  $\text{S}^2 \text{m}^2 \text{mol}^{-2}$

**Sol. (B)**  $S \propto \frac{AC}{\ell}$ ,  $S = K \frac{AC}{\ell} \Rightarrow K = \frac{S\ell}{AC} = \frac{\text{S m}}{\text{m}^2} \frac{\text{m}^3}{\text{mole}} = \text{S(mole)}^{-1} \text{m}^2$

**Ex.39** Passage of three faraday of charge through aqueous solution of  $\text{AgNO}_3$ ,  $\text{CuSO}_4$ ,  $\text{Al(NO}_3)_3$  and  $\text{NaCl}$  respectively will deposit the metals in the ratio (molar).

- (A) 1 : 2 : 3 : 1 (B) 6 : 3 : 2 : 6 (C) 6 : 3 : 0 : 0 (D) 3 : 2 : 1 : 0

**Sol. (C)** 3 eq. of Ag and Cu, zero equivalent of Na and Al will be deposited.

Note electrolysis of  $\text{NaCl}_{\text{aq.}}$  and  $\text{AlCl}_{3\text{aq.}}$  does not give Na and Al metal at cathode.

Thus molar ratio is  $\frac{3}{1} : \frac{3}{2}$  for Ag : Cu

or  $3 : \frac{3}{2}$  or 6 : 3 : 0 : 0 for Ag : Cu : Al : Na

**Ex.40**  $E_{\text{Fe}^{2+}/\text{Fe}}^{\circ}$  and  $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ}$  are  $-0.441 \text{ V}$  and  $0.771 \text{ V}$  respectively,  $E^{\circ}$  for the reaction.

$\text{Fe} + 2\text{Fe}^{3+} \longrightarrow 3\text{Fe}^{2+}$ , will be.

- (A) 1.212 V (B) 0.111 V (C) 0.330 V (D) 1.653 V

**Sol. (A)**  $E_{\text{cell}}^{\circ} = E_{\text{Fe}/\text{Fe}^{2+}}^{\circ} + E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ}$   
 $= 0.441 + 0.771 = 1.212 \text{ V}$

**Ex.41** Efficiency of a cell with cell reaction under standard conditions,

$\text{A}_{(\text{s})} + \text{B}^{+} \longrightarrow \text{A}^{+} + \text{B}_{(\text{s})}$ ;  $\Delta H^{\circ} = -300 \text{ kJ}$  is 70%. The standard electrode potential of cell is.

- (A) 2.176 V (B) +2.876 V (C) 1.248 V (D) +1.648 V

**Sol. (A)** Efficiency =  $\frac{\Delta G^{\circ}}{\Delta H^{\circ}} = \frac{-nE^{\circ}F}{\Delta H^{\circ}}$ ,  $E^{\circ} = \frac{\text{Efficiency} \times \Delta H^{\circ}}{-nF} = \frac{70 \times (-300 \times 10^3)}{100 \times (-1) \times 96500} = 2.176 \text{ V}$

**Ex.42**  $E^{\circ}$  for  $\text{F}_2 + 2\text{e} \rightleftharpoons 2\text{F}^{-}$  is 2.7 V. Thus  $E^{\circ}$  for  $\text{F}^{-} \rightleftharpoons \frac{1}{2}\text{F}_2 + \text{e}$  is.

- (A) 1.35 V (B) - 1.35 V (C) - 2.7 V (D) 2.7 V

**Sol. (C)**  $E_{\text{OP}}^{\circ} = -E_{\text{RP}}^{\circ}$

**Ex.43** Salts of A (atomic weight 7), B (atomic weight 27) and C (atomic weight 48) were electrolysed under identical condition using the same quantity of electricity. It was found that when 2.1 g of A was deposited, the weights of B and C

deposited were 2.7 and 7.2 g. The valencies of A, B and C respectively.

- (A) 3, 1 and 2      (B) 2, 6 and 3      (C) 3, 1 and 3      (D) 2, 3 and 2

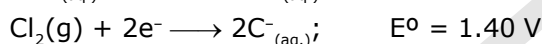
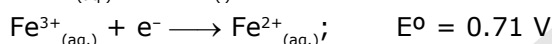
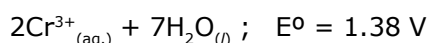
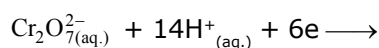
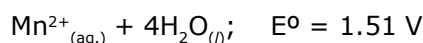
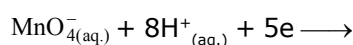
**Sol.** (B)  $\text{gm EqA} = \text{gm Eq B} = \text{gm EqC}$

$$\frac{2.1}{x} = \frac{2.7}{y} = \frac{7.2}{z}, \quad 0.3x = 0.1y = 0.15z$$

$$3x = y = 1.5z$$

$$x = 2, y = 6, z = 3$$

**Ex.44** Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below:



Identify the only incorrect statement regarding the quantitative estimation of aqueous  $\text{Fe}(\text{NO}_3)_2$ .

- (A)  $\text{MnO}_4^-$  can be used in aqueous HCl      (B)  $\text{Cr}_2\text{O}_7^{2-}$  can be used in aqueous HCl  
(C)  $\text{MnO}_4^-$  can be used in aqueous  $\text{H}_2\text{SO}_4$       (D)  $\text{Cr}_2\text{O}_7^{2-}$  can be used in aqueous  $\text{H}_2\text{SO}_4$

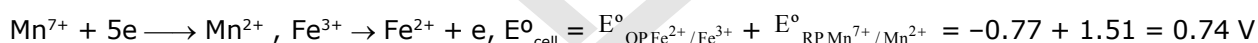
**Sol.** (A)  $\text{MnO}_4^-$  will oxidise  $\text{Cl}^-$  ion according to equation



$$\text{Thus } E^\circ_{\text{cell}} = E^\circ_{\text{OPCl}^-/\text{Cl}_2} + E^\circ_{\text{RPMn}^{7+}/\text{Mn}^{2+}} = -1.40 + 1.51 = 0.11 \text{ V}$$

or reaction is feasible.

$\text{MnO}_4^-$  will oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$



or reaction is feasible

Thus  $\text{MnO}_4^-$  will not oxidize only  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  in aqueous HCl but it will also oxidise  $\text{Cl}^-$  to  $\text{Cl}_2$ . Suitable oxidant should not oxidise  $\text{Cl}^-$  to  $\text{Cl}_2$  and should oxidise only  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  in redox titration.

**Ex.45** The emf of the cell  $\text{Zn} | \text{Zn}^{2+} (0.01\text{M}) || \text{Fe}^{2+} (0.001\text{M}) | \text{Fe}$  at 298 K is 0.2905, then the value of equilibrium constant for the reaction is.

- (A)  $e^{0.32/0.0295}$       (B)  $10^{0.32/0.0295}$       (C)  $10^{0.26/0.0295}$       (D)  $10^{0.32/0.0591}$

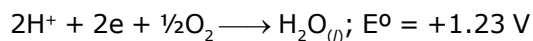
**Sol.** (B)  $\text{Zn} + \text{Fe}^{2+} \longrightarrow \text{Fe} + \text{Zn}^{2+}$

$$E_{\text{cell}} = E^\circ_{\text{cell}} + \frac{0.059}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{Zn}^{2+}]}, \quad 0.2905 = E^\circ_{\text{cell}} + \frac{0.059}{2} \log \frac{0.001}{0.01}$$

$$\therefore E^\circ_{\text{cell}} = 0.2905 + 0.0295 = 0.32 \text{ V}, \quad \text{Now } E^\circ_{\text{cell}} = \frac{0.059}{2} \log_{10} K_c, \quad 0.32 = \frac{0.059}{2} \log_{10} K_c$$

$$\therefore K_c = 10^{0.32/0.0295}$$

**Ex.46** The rusting of iron takes place as follows :



The  $\Delta G^\circ$  for the net process is.

- (A)  $-322 \text{ kJ mol}^{-1}$  (B)  $-161 \text{ kJ mol}^{-1}$  (C)  $-152 \text{ kJ mol}^{-1}$  (D)  $-76 \text{ kJ mol}^{-1}$

**Sol.** (A)  $E^\circ_{\text{cell}} = E^\circ_{\text{OPFe}} + E^\circ_{\text{RPH}_2\text{O}} = 0.44 + 1.23 = 1.67 \text{ V}$

$$\therefore \Delta G^\circ = -nE^\circ F = -2 \times 1.67 \times 96500 \text{ J} = -322.31 \text{ kJ mol}^{-1}$$

### Passage : (Q.47 to 52)

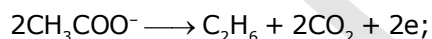
Electrolysis involves electronation and de-electronation at the respective electrodes. Anode of electrolytic cell is the electrode at which de-electronation takes place whereas at cathode electronation is noticed. If two or more ions of same charge are to be electronated or de-electronated, the ion having lesser discharge potential is discharged. Discharge potential of an ion refers for  $E^\circ_{\text{OP}}$  or  $E^\circ_{\text{RP}}$  as the case may be. The products formed at either electrode is given in terms of Faraday's laws of

electrolysis i.e.,  $w = \frac{E_{\text{it}}}{96500} \cdot$

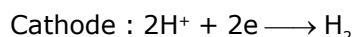
**Ex.47** During electrolysis of  $\text{CH}_3\text{COONa}_{(\text{aq.})}$ , the mole ratio of gases formed at cathode and anode is.

- (A) 1 : 2 (B) 2 : 1 (C) 3 : 1 (D) 1 : 3

**Sol.** (D) Anode :



3 mole

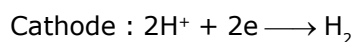


1 mole

**Ex.48** During electrolysis of  $\text{HCOONa}_{(\text{aq.})}$ , the gas liberated at anode and cathode are respectively.

- (A)  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{H}_2$  (B)  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{O}_2$  (C)  $\text{H}_2$  and  $\text{O}_2$  (D)  $\text{O}_2$  and  $\text{H}_2$

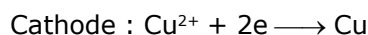
**Sol.** (A) Anode :  $2\text{HCOO}^- \longrightarrow \text{H}_2 + 2\text{CO}_2 + 2\text{e}^-;$



**Ex.49** During electrolysis of  $\text{CuSO}_4_{(\text{aq.})}$ , the pH of solution becomes.

- (A)  $< 7$  (B)  $> 7$  (C)  $= 7$  (D)  $\geq 7$

**Sol.** (A) Anode :  $2\text{OH}^- \longrightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2\text{e}^-;$

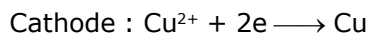


$[\text{OH}^-]$  decreases, thus pH decrease i.e.  $< 7$ .

**Ex.50** 5 litre solution of 0.4 M  $\text{CuSO}_{4(\text{aq.})}$  is electrolysed using Cu electrode. A current of 482.5 ampere is passed for 4 minute. The concentration of  $\text{CuSO}_4$  left in solution is.

- (A) 0.16 M                      (B) 0.32 M                      (C) 0.34 M                      (D) 0.40 M

**Sol.** (D) It is the case of attacked electrodes that is



Thus no change in conc. of  $\text{Cu}^{2+}$  ions.

**Ex.51** 5 litre solution of 0.4 M  $\text{Ni}(\text{NO}_3)_2$  is electrolysed using Pt electrodes with 2.4125 ampere current for 10 hour.

- (A) 0.31 M                      (B) 0.22 M                      (C) 0.26 M                      (D) 0.40 M

**Sol.** (A) Eq. of  $\text{Ni}(\text{NO}_3)_2 = 5 \times 0.4 \times 2 = 4$ ;

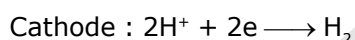
$$\text{Eq. of Ni}^{2+} \text{ lost} = \frac{\text{i.t.}}{96500} = \frac{2.4125 \times 10 \times 60 \times 60}{96500} = 0.9$$

$$\therefore \text{Eq. of Ni}(\text{NO}_3)_2 \text{ left} = 4 - 0.9 = 3.1, \quad \therefore \text{Molarity of Ni}(\text{NO}_3)_2 = \frac{3.1}{5 \times 2} = 0.31$$

**Ex.52** The volume of octane required to be used for its combustion by the oxygen liberated during electrolysis of an  $\text{NaNO}_{3(\text{aq.})}$  by passing 9.65 ampere current for 1 hr. is.

- (A) 322.56 mL                      (B) 32.256 mL                      (C) 3.22 mL                      (D)  $1.612 \times 10^2$  mL

**Sol.** (D) Anode :  $2\text{OH}^- \longrightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2\text{e}^-$ ;



$$\text{Eq. of O}_2 \text{ formed} = \frac{9.65 \times 10 \times 60 \times 60}{96500} = 0.36$$

$$\therefore \text{Mole of O}_2 \text{ formed} = \frac{0.36}{4} = 0.09, \quad \text{C}_8\text{H}_{18} + \frac{25}{2} \text{O}_2 \longrightarrow 8\text{CO}_2 + 9\text{H}_2\text{O}$$

$$\therefore \text{Mole of C}_8\text{H}_{18} = \frac{25}{2} \times 0.09 = 7.2 \times 10^{-3}, \quad \therefore V_{\text{C}_8\text{H}_{18}} = 7.2 \times 10^{-3} \times 22400 = 161.2 \text{ mL}$$

**Ex.53** The specific conductivity of 0.02 M KCl solution at  $25^\circ\text{C}$  is  $2.768 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The resistance of this solution at  $25^\circ\text{C}$  when measured with a particular cell was 250.2 ohm. The resistance of 0.01 M  $\text{CuSO}_4$  solution at  $25^\circ\text{C}$  measured with the same cell was 8331 ohm. Calculated the molar conductivity of the copper sulphate solution.

$$\text{Sol. Cell constant} = \frac{\text{Sp.cond.of KCl}}{\text{Conductance of KCl}} = \frac{2.768 \times 10^{-3}}{1/250.2} = 2.768 \times 10^{-3} \times 250.2$$

For 0.01 M  $\text{CuSO}_4$  solution

$$\text{Sp. conductivity} = \text{Cell constant} \times \text{Conductance} = 2.768 \times 10^{-3} \times 250.2 \times \frac{1}{8331}$$



$$\text{Molar conductance} = \text{Sp. cond.} \times \frac{1000}{C} = \frac{2.768 \times 10^{-3} \times 250.2}{8331} \times \frac{1000}{1/100} = 8.312 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

**Ex.54** A decinormal solution of NaCl has specific conductivity equal to 0.0092. If ionic conductances of  $\text{Na}^+$  and  $\text{Cl}^-$  ions at the same temperature are 43.0 and 65.0  $\text{ohm}^{-1}$  respectively. Calculate the degree of dissociation of NaCl solution

**Sol.** Equivalent conductance of N/10 NaCl solution

$$\Lambda_v = \text{Sp. conductivity} \times \text{dilution} = 0.0092 \times 10,000 = 92 \text{ ohm}^{-1}$$

$$\Lambda_\infty = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} = 43.0 + 65.0 = 108 \text{ ohm}^{-1}$$

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{92}{108} = 0.85$$

**Ex.55** The specific conductance of saturated solution of AgCl is found to be  $1.86 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$  and that of water is  $6 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The solubility of AgCl is ....

$$\text{Given, } \Lambda_{\text{AgCl}}^\circ = 137.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

$$(A) 1.7 \times 10^{-3} \text{ M} \quad (B) 1.3 \times 10^{-5} \text{ M} \quad (C) 1.3 \times 10^{-4} \text{ M} \quad (D) 1.3 \times 10^{-6} \text{ M}$$

**Sol.**  $k_{\text{AgCl}} = k_{\text{AgCl (Solution)}} - k_{\text{H}_2\text{O}} = 1.86 \times 10^{-6} - 6 \times 10^{-8} = 1.8 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$

$$\Lambda_{\text{AgCl}}^\circ = k \times \frac{1000}{S}, \quad \therefore S = \frac{k \times 1000}{\Lambda_{\text{AgCl}}^\circ} = \frac{1.8 \times 10^{-6} \times 1000}{137.2} = 1.31 \times 10^{-5} \text{ M}$$

**Ex.56** Resistance of a solution (A) is 50 ohm and that of solution (B) is 100 ohm, both solution being taken in the same conductivity cell. If equal volumes of solution (A) and (B) are mixed, what will be the resistance of the mixture, using the same cell? Assume that there is no increase in the degree of dissociation of (A) and (B) mixing.

**Sol.** Let us suppose  $k_1$  and  $k_2$  are the specific conductance of solutions 'A' and 'B' respectively and cell constant is 'y'. We know that,  
Specific conductance = Conductance  $\times$  Cell constant

$$\text{For (A), } k_1 = \frac{1}{50} \times y \quad \text{For (B), } k_2 = \frac{1}{100} \times y$$

When equal volume of (A) and (B) are mixed, the volume becomes double. Then,

$$\text{Specific conductance of mixture} = \frac{k_1 + k_2}{2}$$

$$\therefore \frac{k_1 + k_2}{2} = \frac{1}{R} \times y \quad \frac{1}{2} \left[ \frac{y}{50} + \frac{y}{100} \right] = \frac{1}{R} \times y \quad \frac{1}{100} + \frac{1}{200} = \frac{1}{R}$$

$$R = 200/3 = 66.66 \text{ ohm}$$

**Ex.57** A big irregular shaped vessel contained water, specific conductance of which was  $2.56 \times 10^{-5} \text{ mho cm}^{-1}$ , 500 g of NaCl was then added to the water and the specific conductance after the addition of NaCl was found to be  $3.1 \times 10^{-5} \text{ mho cm}^{-1}$ . Find the capacity of the vessel if it was fully filled with water. ( $\Lambda^\circ \text{ NaCl} = 149.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ )

**Sol.** Let us suppose the volume of vessel is V mL

$$\text{Volume containing 1 equivalent} = \frac{\text{Volume}}{\text{Mass/equivalent mass}} = \frac{V}{500/58.5} = \frac{V}{8.547}$$

$$\begin{aligned} \text{Specific conductance of NaCl} &= \text{Specific conductance of NaCl solution} - \text{Specific conductance of water} \\ &= 3.1 \times 10^{-5} - 2.56 \times 10^{-5} = 0.54 \times 10^{-5} \text{ mho cm}^{-1} \end{aligned}$$

$$\Lambda = k \times \text{volume containing 1 equivalent of electrolyte} \quad \dots(i)$$

For very dilute solution, when the big vessel is fully filled

$$\Lambda_{\text{NaCl}}^{\infty} = 149.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}, \text{ Thus, from eq. (i) } 149.9 = 0.54 \times 10^{-5} \times \frac{V}{8.547}$$

$$V = 237258.38 \text{ L}$$

**Ex.58** Maximum Conductivity would be of –

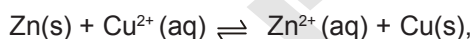
- (A)  $\text{K}_3\text{Fe}(\text{CN})_6$  [0.1 M solution]                      (B)  $\text{K}_2\text{Ni}(\text{CN})_4$  [0.1M solution]  
 (C)  $\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  [0.1 M solution] (D)  $\text{Na}[\text{Ag}(\text{S}_2\text{O}_3)_3]$  [0.1 M solution]

**Sol.** (C)

Double salt on ionization gives more ions. One molecule of the salt gives  $\text{Fe}^{+2}$ ,  $2\text{Al}^{+3}$ ,  $4\text{SO}_4^{-2}$  ions. Hence its conductance would be highest.

### Discussion Questions

(i) For the reaction given below, apply Le-Chatelier principle to justify the results recorded by you and also bring out mathematical rationalisation of your results.



(ii) Determine the slope of the graph. Match experimental value with the theoretical value. On what factors does the value of slope depend?

(iii) Devise another experiment to study the variation in cell potential with concentration of one of the ions involved in a cell reaction.

(iv) What factor is kept in mind while selecting an electrolytic solution for the construction of a salt bridge?

(v) Is it possible to measure the single electrode potential?

## Class Room Problems

**Based on Electrolysis**

- 1 A current of 3.7 ampere is passed for 6 hr between Ni electrodes in 0.5 litre of 2M solution of  $\text{Ni}(\text{NO}_3)_2$ . What will be the molarity of solution at the end of electrolysis ?

Sol. [2M]

- 3 50 mL of 0.1 M  $\text{CuSO}_4$  solution is electrolysed using Pt electrodes with a current of 0.965 ampere for a period of 1 minute. Assuming that volume of solution does not change during electrolysis, calculate  $[\text{Cu}^{2+}]$ ,  $[\text{H}^+]$  and  $[\text{SO}_4^{2-}]$  after electrolysis. What will be the concentration of each species if current is passed using Cu electrodes ?

Sol.  $[\text{Cu}^{+2}] = 0.04\text{M}$ ,  
 $\text{H}^+ = 0.12\text{ M}$   
 $\text{SO}_4^{2-} = 0.1\text{ M}$

- 2 A Zn rod weighing 25g was kept in 100 mL of 1M  $\text{CuSO}_4$  solution. After a certain time the molarity of  $\text{Cu}^{2+}$  in solution was 0.8. What was molarity of  $\text{SO}_4^{2-}$  ? What was the weight of Zn rod after cleaning ? (At. weight of Zn = 65.4)

Sol. [23.69 gm Zn left]

- 4 An electric current is passed through two electrolytic cells connected in series, one containing  $\text{AgNO}_3(\text{aq})$  and other  $\text{H}_2\text{SO}_4(\text{aq})$ . What volume of  $\text{O}_2$  measured at  $25^\circ\text{C}$  and 750 mm in Hg would be liberated from  $\text{H}_2\text{SO}_4$  if :
- (a) 1 mole of  $\text{Ag}^+$  are deposited from  $\text{AgNO}_3$  solution ?
- (b)  $8 \times 10^{22}$  ions of  $\text{Ag}^+$  are deposited from  $\text{AgNO}_3$  solution ?

**Sol.** [(a) 1/4 litre, (b) 6.25 litre]

**Sol.** [158.1 ml]

- 5** A current of 1.70 A is passed through 300 mL of 0.160 M solution of  $\text{ZnSO}_4$  for 230 sec. with a current efficiency of 90% Find the molarity of  $\text{Zn}^{2+}$  after the deposition of Zn. Assume the volume of the solution remains constant during electrolysis.

**Sol.** [ 0.15 litre ]

**Based on Electrochemical cell**

- 7** (a) If  $E^0(\text{Ag}^+/\text{Ag}) = 0.8 \text{ V}$  and  $E^0(\text{H}^+/\text{H}_2) = 0 \text{ V}$ , in a cell arrangement using these two electrodes, which will act as anode cathode ? Also find the  $E^0$  of the cell.  
 (b) Construct a cell using given electrodes at  $25^\circ\text{C}$ . Find its standard EMF.  
 $E^0(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$  and  
 $E^0(\text{Cu}^{2+}/\text{Cu}) = 0.338 \text{ V}$

**Sol.** [1.148 V]

- 6** An acidic solution of  $\text{Cu}^{2+}$  salt containing 0.4 g of  $\text{Cu}^{2+}$  is electrolysed until all the Cu is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept of 100 ml and the current at 1.2 ampere. Calculate volume of gases evolved at NTP during entire electrolysis. (At. wt. of Cu = 63.6)

- 8 The dry cell (flash light battery) used to power flashlights, clocks, radios etc follows following reaction.  $\text{Zn(s)} + 2 \text{MnO}_2\text{(s)} + 8 \text{NH}_4^+ \rightarrow \text{Zn}^{2+} + 2 \text{Mn}^{3+} + 4 \text{H}_2\text{O} + 8 \text{NH}_3$   
Write anode and cathode reactions.

Sol.

1.  $\text{Fe}/\text{Fe}(\text{NO}_3)_2 (1.0 \text{ M}) \parallel \text{Zn}^{2+} (1.0 \text{ M})/\text{Zn}$
2.  $\text{Pt}/\text{Cl}_2(\text{g})/\text{KCl} \parallel \text{Hg}_2\text{Cl}_2(\text{s})/\text{Hg}$
3.  $\text{Cd}/\text{Cd}^{2+} (1.0 \text{ M}) \parallel \text{AgNO}_3/\text{Ag}$   
 $E^0 (\text{Fe}) = 0.41 \text{ V}; E^0 (\text{Cd}) = 0.40 \text{ V}; E^0 (\text{Zn}) = 0.76 \text{ V}$   
 $E^0 (\text{Cl}^- / \text{Cl}_2) = -1.36 \text{ V}; E^0 (\text{Ag}) = -0.80 \text{ V}$   
 $; E^0 (\text{Hg}/\text{Hg}_2\text{Cl}_2) = -0.27 \text{ V}$

Sol. [(1) 0.35 V (2) -1.09 V (3) -1.2 V]

- 10 Find the electrode potentials of the following electrodes.

- (a)  $\text{Pt}, \text{H}_2(1 \text{ atm})/\text{HCl} (0.1 \text{ M}),$
- (b)  $\text{Pt}, \text{H}_2(2 \text{ atm})/\text{H}_2\text{SO}_4 (0.01 \text{ M})$

Sol. [(a) 0.059 (b) 0.109 V]

- 9 For each of the following cells :

- (a) Write the equation for cell process.
- (b) Find  $E^0$  for each cell.
- (c) Explain the significance of any negative answers in part (b).

- 11** For the cell :  $\text{Zn}/\text{Zn}^{2+} (x\text{M}) \parallel \text{Ag}^+/\text{Ag} (y\text{M})$   
 (a) Write Nernst Equation to show that how  $E(\text{cell})$  vary with concentration of  $\text{Zn}^{2+}$  and  $\text{Ag}^+$  ions.  
 (b) Find  $E(\text{cell})$  for  $[\text{Zn}^{2+}] = 0.01\text{M}$  and  $[\text{Ag}^+] = 0.05\text{M}$

**Sol.** [1.56 V]

- 12** In the cell arrangement of above questions, for what value of  $Q$  i.e., the ratio of  $[\text{Zn}^{2+}]$  to that of  $[\text{Ag}^+]^2$ , will the cell EMF be :  
 (a) 1.0 V, (b) 0.0 V

**Sol.**

**Sol.** [1.7 × 10<sup>14</sup>]

- 15** A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of  $10^{-6}\text{M}$   $\text{H}^+$  ions. The EMF of the cell is 0.118 V at 25 °C. Calculate the concentration of hydrogen ions at the positive electrode.

**Sol.** ( $[\text{H}^+]_{\text{cathode}} = 10^{-4}\text{M}$ )

- 13** If excess of Zn is added to 1.0M solution of  $\text{CuSO}_4$ , find the concentration of  $\text{Cu}^{2+}$  ions at equilibrium. The standard reduction potentials of Zn and Cu at 25 °C are 0.76 V and +0.34V.

- 16** Find the standard electrode potential of  $\text{MnO}_4^- / \text{MnO}_2$ . The standard electrode potentials of  $\text{MnO}_4^- / \text{Mn}^{2+} = 1.51\text{V}$  and  $\text{MnO}_2 / \text{Mn}^{2+} = 1.23\text{V}$ .

**Sol.****Sol.**

- 17** E.M.F. of following cell is 0.265 V at 25 °C and 0.2595 V at 35 °C. Calculate heat of the reaction taking place at 25 °C  $\text{Pt}(\text{H}_2) \mid \text{HCl}(\text{g}) \parallel \text{AgCl} \mid \text{Ag}(\text{s})$

**Sol.**

- 19** Calculate the electrode potential at 25 °C of  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$  electrode at  $\text{pOH} = 11$  in a solution of 0.01 M both in  $\text{Cr}^{3+}$  and  $(\text{Cr}_2\text{O}_7^{2-}) = 1.33$  V. If this electrode is coupled with a hydrogen gaseous electrode at  $\text{pH} = 6$ , find the emf of the spontaneous cell.

**Sol.**

- 18** Calculate the EMF of the following cell at 25 °C,  $\text{Pt}, \text{H}_2(1 \text{ atm}) / \text{H}^+(0.09 \text{ M}) \parallel \text{OH}^-(0.075 \text{ M}) / \text{H}_2(1 \text{ atm}), \text{Pt}$  ( $K_w$  of  $\text{H}_2\text{O} = 1 \times 10^{-14}$ )

- 20 Find the  $K_{sp}$  of  $AgCl$  from the following data. The standard electrode potential of  $Ag/AgCl/Cl^-$  is 0.222 V and  $Ag^+/Ag$  is 0.799 V.

Sol.

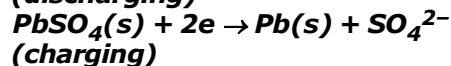
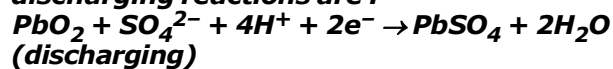
Sol.

$[4.6 \times 10^{-3} m]$

- 21 The standard reduction potential of  $Ag^+/Ag$  electrode at 298 K is 0.799 volts.  $K_{sp}$  of  $AgI = 8.7 \times 10^{-17}$ . Find the electrode potential of  $Ag^+/Ag$  in a saturated solution of  $AgI$ . Also, calculate standard reduction potential of  $I^-/AgI/Ag$  electrode.

Sol.

- 23 During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 g/m to 1.139 g/m. Sulphuric acid of density 1.294 g/m was 39%  $H_2SO_4$  by wt. while acid of density 1.139 g/m contains 20% acid by wt. The battery holds 3.5 L of acid and the value remained practically same through the discharge. Calculate the number of amp/hr for which the battery must have been used. The charging and discharging reactions are :



Sol.

$[0.954 A]$

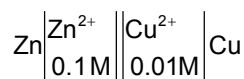
- 22 Two Daniel cells contain the same solution of  $ZnSO_4$  but differ in the  $CuSO_4$  solution. The emf of the cell containing 0.5 M  $CuSO_4$  is higher than the other cell by 0.06V. Calculate the concentration of  $CuSO_4$  in the other cell.



- 24 A test for complete removal of  $\text{Cu}^{2+}$  ions from a solution of  $\text{Cu}^{2+}$  (aq) is to add  $\text{NH}_3(\text{aq})$ . A blue colour signifies the formation of complex  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  having  $K_f = 1.1 \times 10^{13}$  and thus confirms the presence of  $\text{Cu}^{2+}$  in solution. 250 mL of 0.1 M  $\text{CuSO}_4$  (aq.) is electrolysed by passing a current of 3.512 ampere for 1368 second. After passage of this charge sufficient quantity of  $\text{NH}_3(\text{aq})$  is added to electrolysed solution maintaining  $[\text{NH}_3] = 0.10$  M. If  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is detectable upto its concentration as low as  $1 \times 10^{-5}$ , would a blue colour be shown by the electrolysed solution on addition of  $\text{NH}_3$ ?

Sol.

- 25 A graph is plotted between  $E_{\text{cell}}$  and  $\log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$ . The curve was linear with intercept on  $E_{\text{cell}}$  axis equal to 1.10 V. Calculate  $E_{\text{cell}}$  for



Sol.

[1.0705 V]

## Exercise - I

## OBJECTIVE PROBLEMS (JEE MAIN)

1. The passage of current through a solution of certain electrolyte results in the evolution of  $H_2$  at cathode and  $Cl_2$  at anode. The electrolytic solution is -  
(A) Water (B)  $H_2SO_4$   
(C) A NaCl (D) A  $CuCl_2$

Sol.

2. In an electrolytic cell current flows from -  
(A) Cathode to anode in outer circuit  
(B) Anode to cathode outside the cell  
(C) Cathode to anode inside the cell  
(D) Anode to cathode inside the cell

Sol.

3. When an aqueous solution of  $H_2SO_4$  is electrolysed, the ion discharged at anode is -  
(A)  $H^+$  (B)  $OH^-$  (C)  $SO_4^{2-}$  (D)  $O^{2-}$

Sol.

4. 1 mole of Al is deposited by X coulomb of electricity passing through aluminium nitrate solution. The number of moles of silver deposited by X coulomb of electricity from silver nitrate solution is -  
(A) 3 (B) 4 (C) 2 (D) 1

Sol.

5. A solution of  $Na_2SO_4$  in water is electrolysed using Pt electrodes. The products at the cathode and anode are respectively -  
(A)  $H_2$ ,  $SO_2$  (B)  $O_2$ , NaOH  
(C)  $H_2$ ,  $O_2$  (D)  $O_2$ ,  $SO_2$

Sol.

6. In electrolysis of a fused salt, the weight deposited on an electrode will not depend on -  
(A) Temperature  
(B) Current intensity  
(C) Electrochemical equivalent of ions  
(D) Time for electrolysis

Sol.

7. The electrolysis of a solution resulted in the formation of  $H_2$  at the cathode and  $Cl_2$  at the anode. The liquid is -  
(A) Pure water  
(B)  $H_2SO_4$  solution  
(C) NaCl solution in water  
(D)  $CuCl_2$  solution in water

Sol.

8. Which loses charge at cathode -  
(A) Ions  
(B) Cations  
(C) Anions  
(D) Both anions and cations

Sol.

9. In the electrolysis of  $\text{CuSO}_4$ , the reaction :  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ , takes place at :  
 (A) Anode (B) Cathode  
 (C) In solution  
 (D) None

Sol.

10. If mercury is used as cathode in the electrolysis of aqueous  $\text{NaCl}$  solution, the ions discharged at cathode are-  
 (A)  $\text{H}^+$  (B)  $\text{Na}^+$   
 (C)  $\text{OH}^-$  (D)  $\text{Cl}^-$

Sol.

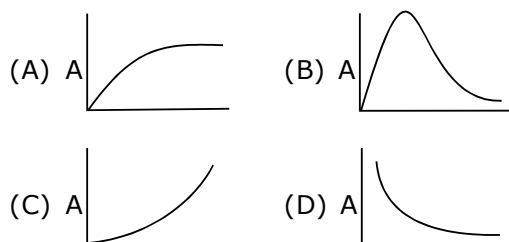
11. The specific conductance of a solution is  $0.3568 \text{ ohm}^{-1}$ . When placed in a cell the conductance is  $0.0268 \text{ ohm}^{-1}$ . The cell constant is-  
 (A)  $1.331 \text{ cm}^{-1}$  (B)  $13.31 \text{ cm}^{-1}$   
 (C)  $0.665 \text{ cm}^{-1}$  (D)  $6.65 \text{ cm}^{-1}$

Sol.

12. A conductance cell was filled with a  $0.02 \text{ M}$   $\text{KCl}$  solution which has a specific conductance of  $2.768 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ . If its resistance is  $82.4 \text{ ohm}$  at  $25^\circ\text{C}$ , the cell constant is-  
 (A)  $0.2182 \text{ cm}^{-1}$  (B)  $0.2281 \text{ cm}^{-1}$   
 (C)  $0.2821 \text{ cm}^{-1}$  (D)  $0.2381 \text{ cm}^{-1}$

Sol.

13. The variation of equivalent conductance vs decrease in concentration of a strong electrolyte is correctly given in the plot -



Sol.

14. Which of the following solutions has the highest equivalent conductance ?  
 (A)  $0.01 \text{ M NaCl}$  (B)  $0.050 \text{ M NaCl}$   
 (C)  $0.005 \text{ M NaCl}$  (D)  $0.02 \text{ M NaCl}$

Sol.

15. The resistance of  $0.01 \text{ N}$  solution of an electrolyte  $\text{AB}$  at  $328 \text{ K}$  is  $100 \text{ ohm}$ . The specific conductance of solution is (cell constant =  $1 \text{ cm}^{-1}$ )-  
 (A)  $100 \text{ ohm}$   
 (B)  $10^{-2} \text{ ohm}^{-1}$   
 (C)  $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$   
 (D)  $10^2 \text{ ohm-cm}$

Sol.

16. For an electrolytic solution of  $0.05 \text{ mol L}^{-1}$ , the conductivity has been found to be  $0.0110 \text{ Scm}^{-1}$ . The molar conductivity is-
- (A)  $0.055 \text{ S cm}^2 \text{ mol}^{-1}$   
 (B)  $550 \text{ S cm}^2 \text{ mol}^{-1}$   
 (C)  $0.22 \text{ S cm}^2 \text{ mol}^{-1}$   
 (D)  $220 \text{ S cm}^2 \text{ mol}^{-1}$

Sol.

17. Two electrodes are fitted in conductance cell  $1.5 \text{ cm}$  apart while the area of cross section of each electrode is  $0.75 \text{ cm}^2$ . The cell constant is-
- (A)  $1.125$  (B)  $0.5 \text{ cm}$   
 (C)  $2.0 \text{ cm}^{-1}$  (D)  $0.2 \text{ cm}^{-1}$

Sol.

18. The best conductor of electricity is in  $1\text{M}$  solution of-
- (A)  $\text{CH}_3\text{COOH}$  (B)  $\text{H}_2\text{SO}_4$   
 (C)  $\text{H}_3\text{PO}_4$  (D) Boric acid

Sol.

19. A certain current liberates  $0.504 \text{ g}$  of  $\text{H}_2$  in  $2 \text{ hours}$ . How many grams of copper can be liberated by the same current flowing for the same time in  $\text{CuSO}_4$  solution -
- (A)  $31.8 \text{ g}$  (B)  $16.0 \text{ g}$   
 (C)  $12.7 \text{ g}$  (D)  $63.5 \text{ g}$

Sol.

20. A current of  $2.6 \text{ ampere}$  is passed through  $\text{CuSO}_4$  solution for  $6 \text{ minutes } 20 \text{ seconds}$ . The amount of  $\text{Cu}$  deposited is (At. wt. of  $\text{Cu} = 63.5$ , Faraday =  $96500 \text{ C}$ )-
- (A)  $6.35 \text{ g}$  (B)  $0.635 \text{ g}$   
 (C)  $0.325 \text{ g}$  (D)  $3.175 \text{ g}$

Sol.

21. Three Faradays of electricity are passed through molten  $\text{Al}_2\text{O}_3$ , aqueous solution of  $\text{CuSO}_4$  and molten  $\text{NaCl}$  taken in three different electrolytic cells. The amount of  $\text{Al}$ ,  $\text{Cu}$  and  $\text{Na}$  deposited at the cathodes will be in the ratio of-
- (A)  $1 \text{ mole} : 2 \text{ mole} : 3 \text{ mole}$   
 (B)  $1 \text{ mole} : 1.5 \text{ mole} : 3 \text{ mole}$   
 (C)  $3 \text{ mole} : 2 \text{ mole} : 1 \text{ mole}$   
 (D)  $1 \text{ mole} : 1.5 \text{ mole} : 2 \text{ mole}$

Sol.

22. The quantity of electricity required to liberate  $0.01\text{g}$  equivalent of an element at the electrode is -
- (A)  $9650\text{C}$  (B)  $96500\text{C}$   
 (C)  $965\text{C}$  (D)  $96.5\text{C}$

Sol.

23. The unit of electrochemical equivalent is-
- (A)  $\text{gm ampere}^{-1}$  (B)  $\text{gm/coulomb}$   
 (C)  $\text{gm-ampere}$  (D)  $\text{coulomb/gram}$

**Sol.**

24. One faraday of electricity will liberate one mole of metal from a solution of-  
(A)  $\text{AuCl}_3$  (B)  $\text{CuSO}_4$  (C)  $\text{BaCl}_2$  (D)  $\text{KCl}$

**Sol.**

25. The number of faraday required to generate 1 mole of  $\text{Mg}$  from  $\text{MgCl}_2$  is-  
(A) 1 (B) 2 (C) 3 (D) 4

**Sol.**

26. One gm metal  $\text{M}^{+2}$  was discharged by the passage of  $1.81 \times 10^{22}$  electrons. What is the atomic weight of metal?  
(A) 33.35 (B) 133.4  
(C) 66.7 (D) 55

**Sol.**

27. One mole of electron passes through each of the solution of  $\text{AgNO}_3$ ,  $\text{CuSO}_4$  and  $\text{AlCl}_3$  when  $\text{Ag}$ ,  $\text{Cu}$  and  $\text{Al}$  are deposited at cathode. The molar ratio of  $\text{Ag}$ ,  $\text{Cu}$  and  $\text{Al}$  deposited are  
(A) 1 : 1 : 1 (B) 6 : 3 : 2  
(C) 6 : 3 : 1 (D) 1 : 3 : 6

**Sol.**

28. Salts of A (atomic weight = 7), B (atomic weight = 27) and C (atomic weight = 48) were electrolysed under identical conditions using the same quantity of electricity. It was found that when 2.1 g of A was deposited, the weights of B and C deposited were 2.7 and 7.2 g. The valencies of A, B and C respectively are  
(A) 3, 1 and 2 (B) 1, 3 and 2  
(C) 3, 1 and 3 (D) 2, 3 and 2

**Sol.**

29. The density of  $\text{Cu}$  is  $8.94 \text{ g cm}^{-3}$ . The quantity of electricity needed to plate an area  $10 \text{ cm} \times 10 \text{ cm}$  to a thickness of  $10^{-2} \text{ cm}$  using  $\text{CuSO}_4$  solution would be  
(A) 13586 C (B) 27172 C  
(C) 40758 C (D) 20348 C

**Sol.**

- 30.** During electrolysis of an aqueous solution of sodium sulphate if 2.4 L of oxygen at STP was liberated at anode. The volume of hydrogen at STP, liberated at cathode would be :

(A) 1.2 L (B) 2.4 L  
(C) 2.6 L (D) 4.8 L

**Sol.**

- 31.** During electrolysis of an aqueous solution of  $\text{CuSO}_4$  using copper electrodes, if 2.5 g of Cu is deposited at cathode, then at anode.

(A) 890 ml of  $\text{Cl}_2$  at STP is liberated  
(B) 445 ml of  $\text{O}_2$  at STP is liberated  
(C) 2.5 g of copper is deposited  
(D) a decrease of 2.5 g of mass takes place

**Sol.**

- 32.** The charge required for the oxidation of one mole  $\text{Mn}_3\text{O}_4$  into  $\text{MnO}_4^{2-}$  in presence of alkaline medium is

(A)  $5 \times 96500 \text{ C}$  (B) 96500 C  
(C)  $10 \times 96500 \text{ C}$  (D)  $2 \times 96500 \text{ C}$

**Sol.**

- 33.** A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively.

(A)  $\text{H}_2, \text{O}_2$  (B)  $\text{O}_2, \text{H}_2$   
(C)  $\text{O}_2, \text{Na}$  (D) None

**Sol.**

Sol.

34. When an aqueous solution of lithium chloride is electrolysed using graphite electrodes

- (A)  $\text{Cl}_2$  is liberated at the anode.
- (B) Li is deposited at the cathode
- (C) as the current flows, pH of the solution around the cathode remains constant
- (D) as the current flows, pH of the solution around the cathode decreases.

Sol.

35. A standard hydrogen electrode has zero electrode potential because

- (A) hydrogen is easier to oxidise
- (B) this electrode potential is assumed to be zero
- (C) hydrogen atom has only one electron
- (D) hydrogen is the lightest element.

36. If the pressure of  $\text{H}_2$  gas is increased from 1 atm to 100 atm keeping  $\text{H}^+$  concentration constant at 1 M, the change in reduction potential of hydrogen half cell at  $25^\circ\text{C}$  will be

- (A) 0.059 V
- (B) 0.59 V
- (C) 0.0295 V
- (D) 0.118 V

Sol.

37. The equilibrium constant for the reaction  $\text{Sr(s)} + \text{Mg}^{2+}(\text{aq}) \rightleftharpoons \text{Sr}^{2+}(\text{aq}) + \text{Mg(s)}$  is  $2.69 \times 10^{12}$  at  $25^\circ\text{C}$

The  $E^\circ$  for a cell made up of the  $\text{Sr/Sr}^{2+}$  and  $\text{Mg}^{2+}/\text{Mg}$  half cells

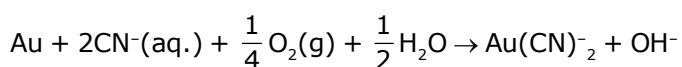
- (A) 0.3667 V
- (B) 0.7346 V
- (C) 0.1836 V
- (D) 0.1349 V

Sol.

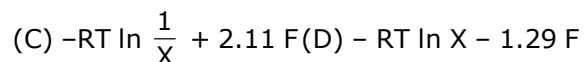
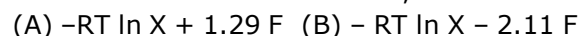
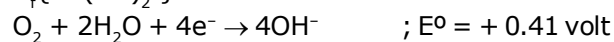
38. A silver wire dipped in 0.1 M HCl solution saturated with AgCl develops oxidation potential of  $-0.25$  V. If  $E_{\text{Ag}/\text{Ag}^+}^0 = -0.799$  V, the  $K_{\text{sp}}$  of AgCl in pure water will be :
- (A)  $2.95 \times 10^{-11}$  (B)  $5.1 \times 10^{-11}$   
 (C)  $3.95 \times 10^{-11}$  (D)  $1.95 \times 10^{-11}$

**Sol.**

39. Consider the reaction of extraction of gold from its ore

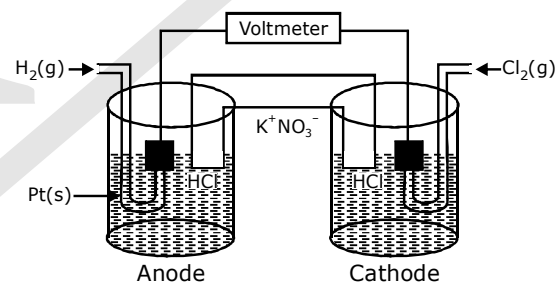


Use the following data to calculate  $\Delta G^0$  for the reaction



**Sol.**

40. Consider the following Galvanic cell.



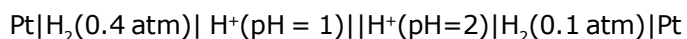
By what value the cell voltage change when concentration of ions in anodic and cathodic compartments both increased by factor of 10 at 298 K.

- (A) + 0.0591 (B) - 0.0591  
 (C) - 0.1182 (D) 0

**Sol.**



41. For the cell



The measured potential at 25° C is

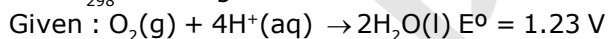
- (A) - 0.1 V (B) - 0.5  
(C) - 0.041 (D) None

Sol.

Sol.

42. For the fuel cell reaction  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$ ;  $\Delta_f H^\circ_{298}(\text{H}_2\text{O}, \text{l}) = -285.5 \text{ kJ/mol}$

What is  $\Delta S^\circ_{298}$  for the given fuel cell reaction ?



- (A) - 0.322 J/K (B) - 0.635 kJ/K  
(C) 3.51 kJ/K (D) - 0.322 kJ/K

Sol.

44. A hydrogen electrode X was placed in a buffer solution of sodium acetate and acetic acid in the ratio a : b and another hydrogen electrode Y was placed in a buffer solution of sodium acetate and acetic acid in the ratio b : a. If reduction potential values for two cells are found to be  $E_1$  and  $E_2$  respectively w.r.t. standard hydrogen electrode, the  $\text{pK}_a$  value of the acid can be given as

- (A)  $\frac{E_1 + E_2}{0.118}$  (B)  $\frac{E_2 - E_1}{0.118}$   
(C)  $-\frac{E_1 + E_2}{0.118}$  (D)  $\frac{E_1 - E_2}{0.118}$

Sol.

43. The standard reduction potentials of  $\text{Cu}^{2+}/\text{Cu}$  and  $\text{Cu}^{2+}/\text{Cu}^+$  are 0.337 and 0.153 V respectively. The standard electrode potential of  $\text{Cu}^+/\text{Cu}$  half cell is :

- (A) 0.184 V (B) 0.827 V  
(C) 0.521 V (D) 0.490 V

45. The resistance of 0.5 M solution of an electrolyte in a cell was found to be  $50 \Omega$ . If the electrodes in the cell are 2.2 cm apart and have an area of  $4.4 \text{ cm}^2$  then the molar conductivity (in  $\text{S m}^2 \text{ mol}^{-1}$ ) of the solution is

- (A) 0.2 (B) 0.02  
(C) 0.002 (D) None of these

Sol.

46. Equivalent conductance of 0.1 M HA (weak acid) solution is  $10 \text{ Scm}^2 \text{ equivalent}^{-1}$  and that at infinite dilution is  $200 \text{ Scm}^2 \text{ equivalent}^{-1}$ . Hence pH of HA solution is
- (A) 1.3 (B) 1.7  
(C) 2.3 (D) 3.7

Sol.

47. If  $x$  is specific resistance of the electrolyte solution and  $y$  is the molarity of the solution, then  $\wedge_m$  is given by :
- (A)  $\frac{1000x}{y}$  (B)  $1000 \frac{y}{x}$   
(C)  $\frac{1000}{xy}$  (D)  $\frac{xy}{1000}$

Sol.

48. The dissociation constant of n-butyric acid is  $1.6 \times 10^{-5}$  and the molar conductivity at infinite dilution is  $380 \times 10^{-4} \text{ Sm}^2 \text{mol}^{-1}$ . The specific conductance of the 0.01 M acid solution is
- (A)  $1.52 \times 10^{-5} \text{ Sm}^{-1}$  (B)  $1.52 \times 10^{-2} \text{ Sm}^{-1}$   
(C)  $1.52 \times 10^{-3} \text{ Sm}^{-1}$  (D) None

Sol.

49. The conductivity of a saturated solution of  $\text{Ag}_3\text{PO}_4$  is  $9 \times 10^{-6} \text{ Sm}^{-1}$  and its equivalent conductivity is  $1.50 \times 10^{-4} \text{ Sm}^2 \text{ equivalent}^{-1}$ . The  $K_{sp}$  of  $\text{Ag}_3\text{PO}_4$  is ;
- (A)  $4.32 \times 10^{-18}$  (B)  $1.8 \times 10^{-9}$   
(C)  $8.64 \times 10^{-13}$  (D) None of these

Sol.

50. A saturated solution in  $\text{AgA}$  ( $K_{sp} = 3 \times 10^{-14}$ ) and  $\text{AgB}$  ( $K_{sp} = 1 \times 10^{-14}$ ) has conductivity of  $375 \times 10^{-10} \text{ Scm}^{-1}$  and limiting molar conductivity of  $\text{Ag}^+$  and  $\text{A}^-$  are  $60 \text{ Scm}^2 \text{mol}^{-1}$  and  $80 \text{ Scm}^2 \text{mol}^{-1}$  respectively then what will be the limiting molar conductivity of  $\text{B}^-$  (in  $\text{Scm}^2 \text{mol}^{-1}$ )
- (A) 150 (B) 180  
(C) 190 (D) 270

Sol.

## Exercise - II

## MULTIPLE CHOICE PROBLEMS(JEE ADVANCED)

1. During discharging of lead storage battery, which of the following is/are true?

(A)  $\text{H}_2\text{SO}_4$  is produced  
 (B)  $\text{H}_2\text{O}$  is consumed  
 (C)  $\text{PbSO}_4$  is formed at both electrodes  
 (D) Density of electrolytic solution decreases

**Sol.**

2. Which of the following arrangement will produce oxygen at anode during electrolysis?

(A) Dilute  $\text{H}_2\text{SO}_4$  solution with Cu electrodes.  
 (B) Dilute  $\text{H}_2\text{SO}_4$  solution with inert electrodes.  
 (C) Fused NaOH with inert electrodes.  
 (D) Dilute NaCl solution with inert electrodes.

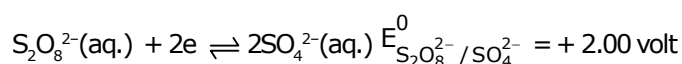
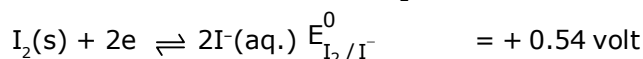
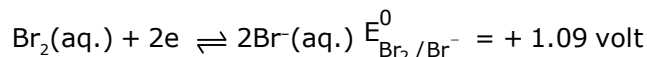
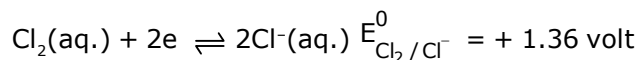
**Sol.**

3. If 270.0 g of water is electrolysed during an experiment performed by miss abhilasha with 75% current efficiency then

(A) 168 L of  $\text{O}_2$  (g) will be evolved at anode at 1 atm & 273 K  
 (B) Total 504 L gases will be produced at 1 atm & 273 K.  
 (C) 336 L of  $\text{H}_2$ (g) will be evolved at anode at 1 atm & 273 K  
 (D) 45 F electricity will be consumed

**Sol.**

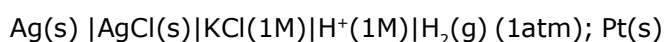
4. Pick out the **correct** statements among the following from inspection of standard reduction potentials (Assume standard state conditions).



(A)  $\text{Cl}_2$  can oxidise  $\text{SO}_4^{2-}$  from solution  
 (B)  $\text{Cl}_2$  can oxidise  $\text{Br}^-$  and  $\text{I}^-$  from aqueous solution  
 (C)  $\text{S}_2\text{O}_8^{2-}$  can oxidise  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  from aqueous solution  
 (D)  $\text{S}_2\text{O}_8^{2-}$  is added slowly,  $\text{Br}^-$  can be reduce in presence of  $\text{Cl}^-$

**Sol.**

5. The EMF of the following cell is 0.22 volt.



Which of the following will decrease the EMF of cell.

(A) increasing pressure of  $\text{H}_2(\text{g})$  from 1 atm to 2 atm  
 (B) increasing  $\text{Cl}^-$  concentration in Anodic compartment  
 (C) increasing  $\text{H}^+$  concentration in cathodic compartment  
 (D) Decreasing KCl concentration in Anodic compartment.

Sol.

**Statement-2** : It is because net cell reaction does not involve active species.

Sol.

8. **Statement-1** : The SRP of three metallic ions  $A^+$ ,  $B^{2+}$ ,  $C^{3+}$  are  $-0.3$ ,  $-0.5$ ,  $0.8$  volt respectively, so oxidising power of ions is  $C^{3+} > A^+ > B^{2+}$

**Statement-2** : Higher the SRP, higher the oxidising power.

Sol.

6. Equal volumes of  $0.015\text{ M CH}_3\text{COOH}$  &  $0.015\text{ M NaOH}$  are mixed together. What would be molar conductivity of mixture if conductivity of  $\text{CH}_3\text{COONa}$  is  $6.3 \times 10^{-4}\text{ S cm}^{-1}$   
 (A)  $8.4\text{ S cm}^2\text{ mol}^{-1}$  (B)  $84\text{ S cm}^2\text{ mol}^{-1}$   
 (C)  $4.2\text{ S cm}^2\text{ mol}^{-1}$  (D)  $42\text{ S cm}^2\text{ mol}^{-1}$

Sol.

9. **Statement-1** : We can add the electrode potential in order to get electrode potential of net reaction.

**Statement-2** : Electrode potential is an intensive property.

Sol.

10. **Statement - I.** In electrolysis, the quantity of electricity needed for depositing 1 mole of silver is different from that required for 1 mole of copper.

**Statement - II.** The atomic weights of silver and copper are different.

Sol.

### Assertion & Reasoning type questions

Each of the questions given below consist of Statement – I and Statement – II. Use the following Key to choose the appropriate answer.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1  
 (B) Statement-1 is true, statement-2 is true and statement - 2 is NOT the correct explanation for statement-1  
 (C) Statement - 1 is true, statement - 2 is false.  
 (D) Statement - 1 is false, statement - 2 is true.

7. **Statement-1** : The voltage of mercury cell remains constant for long period of time.

11. **Statement - I.**  $\text{CuSO}_4$  solution cannot safely be kept in a Zn vessel usual.

**Statement - II.** The position of Zn is lower than Cu in Electro-chemical-series.

Sol.

**12. Statement - I.** Zinc displaces copper from copper sulphate solution..

**Statement - II.** The  $E^\circ$  is Zn of  $-0.76$  volt and that of copper is  $+0.34$  volt.

**Sol.**

**13. Statement - I.** Gold chloride ( $\text{AuCl}_3$ ) solution cannot be stored in a vessel made of copper, iron, nickel, chromium, zinc or tin.

**Statement - II.** Gold is very precious metal.

**Sol.**

**14. Statement - I .** Specific conductance decreases with dilution whereas equivalent conductance increases.

**Statement - II.** On dilution, number of ions per cc decreases but total number of ions increases considerably.

**Sol.**

**15. Statement - I.** Salt bridge is used in Electrochemical cell.

**Statement - II.** The ions of the electrolyte used in salt bridge should have almost same ionic mobility.

**Sol.**

**16. Statement - I.** Absolute value of an electrode potential can not be calculated.

**Statement - II.** Neither oxidation nor reduction can take place alone.

**Sol.**

### Comprehension

#### Paragraph -1

A sample of water from a large swimming pool has a resistance of  $10000\ \Omega$  at  $25^\circ\text{C}$  when placed in a certain conductance cell. When filled with  $0.02\ \text{M}$  KCl solution, the cell has a resistance of  $100\ \Omega$  at  $25^\circ\text{C}$ .  $585\ \text{gm}$  of NaCl were dissolved in the pool, which was thoroughly stirred. A sample of this solution gave a resistance of  $8000\ \Omega$ .

[**Given :** Molar conductance of NaCl at that concentration is  $125\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$  and molar conductivity of KCl at  $0.02\ \text{M}$  is  $200\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ .]

**17.** Cell constant (in  $\text{cm}^{-1}$ ) of conductance cell is :

- (A) 4 (B) 0.4  
(C)  $4 \times 10^{-2}$  (D)  $4 \times 10^{-5}$

**Sol.**

**18.** Conductivity ( $\text{Scm}^{-1}$ ) of  $\text{H}_2\text{O}$  is :

- (A)  $4 \times 10^{-2}$  (B)  $4 \times 10^{-3}$   
(C)  $4 \times 10^{-5}$  (D) None of these

**Sol.**

**19.** Volume (in Litres) of water in the pool is:

- (A)  $1.25 \times 10^5$  (B) 1250  
(C) 12500 (D) None of these

**Sol.**

## Comprehension

## Paragraph -2

Copper reduces  $\text{NO}_3^-$  into NO and  $\text{NO}_2$  depending upon conc. of  $\text{HNO}_3$  in solution. Assuming  $[\text{Cu}^{2+}] = 0.1 \text{ M}$ , and  $P_{\text{NO}} = P_{\text{NO}_2} = 10^{-3} \text{ atm}$  and using given data answer the following questions.

$$E_{\text{Cu}^{2+}/\text{Cu}}^0 = + 0.34 \text{ volt}$$

$$E_{\text{NO}_3^-/\text{NO}}^0 = + 0.96 \text{ volt}$$

$$E_{\text{NO}_3^-/\text{NO}_2}^0 = + 0.79 \text{ volt}$$

$$\text{at } 298 \text{ K } \frac{RT}{F} (2.303) = 0.06 \text{ volt}$$

20.  $E_{\text{Cell}}$  for reduction of  $\text{NO}_3^- \rightarrow \text{NO}$  by  $\text{Cu(s)}$ , when  $[\text{HNO}_3] = 1 \text{ M}$  is [At  $T = 298$ ]

- (A)  $\sim 0.61$  (B)  $\sim 0.71$   
(C)  $\sim 0.51$  (D)  $\sim 0.81$

Sol.

21. At what  $\text{HNO}_3$  concentration thermodynamic tendency for reduction of  $\text{NO}_3^-$  into NO and  $\text{NO}_2$  by copper is same?

- (A)  $10^{1.23} \text{ M}$  (B)  $10^{0.56} \text{ M}$   
(C)  $10^{0.66} \text{ M}$  (D)  $10^{0.12} \text{ M}$

Sol.

## Paragraph -3

The driving force  $\Delta G$  diminishes to zero on the way to equilibrium, just as in any other spontaneous process. Both  $\Delta G$  and the cell potential  $\left(E = -\frac{\Delta G}{nF}\right)$  are zero when the redox reaction comes to equilibrium. The Nernst equation for the redox process of the cell may be given as :

$$E = E^0 - \frac{0.059}{n} \log_{10} Q$$

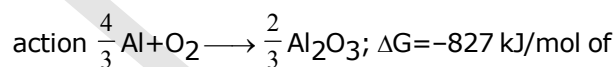
The key to the relationship is the standard cell potential  $E^0$ , derived from the standard free energy change as :

$$E^0 = -\frac{\Delta G^0}{nF}$$

At equilibrium, the Nernst equation is given as :

$$E^0 = \frac{0.059}{n} \log_{10} K$$

22. On the basis of information available for the re-



$\text{O}_2$  the minimum emf required to carry out an electrolysis of  $\text{Al}_2\text{O}_3$  is -

(Given :  $1 \text{ F} = 96500 \text{ C}$ )

- (A) 2.14 V (B) 4.28 V  
(C) 6.42 V (D) 8.56 V

Sol.

23. The equilibrium constant  $K_c$  will be equal to Q when -

- (A)  $E = E^0$  (B)  $RT/nF = 1$   
(C)  $E = 0$  (D)  $E^0 = 1$

**Sol.**

- 24.** The nature of graph of  $E^\circ_{\text{cell}}$  against  $\log K_C$  is a/an -

(A) straight line (B) parabola  
(C) hyperbola (D) elliptical curve

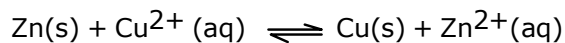
**Sol.**

- 25.** The equilibrium constant  $K_C$  for the reaction:  
 $\text{Cu(s)} + 2\text{Ag}^+(\text{aq}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{Ag(s)}$   
 ( $E^\circ_{\text{cell}} = 0.46\text{V}$ ) will be -  
 (A) antilog 15.6 (B) antilog 2.5  
 (C) antilog 1.5 (D) antilog 12.2

**Sol.**

- 26.**  $E^\circ$  for the electrochemical cell,  
 $\text{Zn(s)} | \text{Zn}^{2+} (1 \text{ M}) \text{ aq} || \text{Cu}^{2+} (1 \text{ M}) \text{ aq} | \text{Cu(s)}$   
 is 1.10 volt at  $25^\circ\text{C}$ .

the equilibrium constant for the cell reaction:



will be -

- (A)  $10^{-37}$  (B)  $10^{37}$   
 (C)  $10^{-39}$  (D)  $10^{39}$

**Sol.**

### Match the Column

#### 27. Column-I

- (A) Dilute solution of HCl  
 (B) Dilute solution of NaCl  
 (C) Concentrated solution of NaCl  
 (D)  $\text{AgNO}_3$  solution

#### Column-II

- (P)  $\text{O}_2$  evolved at anode  
 (Q)  $\text{H}_2$  evolved at cathode  
 (R)  $\text{Cl}_2$  evolved at anode  
 (S) Ag deposition at cathode

**Sol.**

## Exercise - III

## (JEE ADVANCED)

## GALVANIC CELL :

## Representation of Cell diagrams, complete and half cell reactions:

**Q. 1** Write cell reaction of the following cells:

- (a)  $\text{Ag}|\text{Ag}^+(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu}$   
 (b)  $\text{Pt}|\text{Fe}^{2+}, \text{Fe}^{3+}||\text{MnO}_4^-, \text{Mn}^{2+}, \text{H}^+|\text{Pt}$   
 (c)  $\text{Pt}, \text{Cl}_2|\text{Cl}^-(\text{aq})||\text{Ag}^+(\text{aq})|\text{Ag}$   
 (d)  $\text{Pt}, \text{H}_2|\text{H}^+(\text{aq})||\text{Cd}^{2+}(\text{aq})|\text{Cd}$

**Sol.**

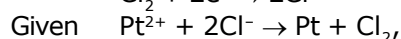
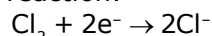
**Sol.**

**Q.2** Write cell representation for following cells.

- (a)  $\text{Cd}^{2+}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cd}(\text{s})$   
 (b)  $2\text{Ag}^+(\text{aq}) + \text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{Ag}(\text{s})$   
 (c)  $\text{Cr}_2\text{O}_7^{2-}(\text{aq.}) + 14\text{H}^+(\text{aq}) + 6\text{Fe}^{2+}(\text{aq}) \rightarrow 6\text{Fe}^{3+}(\text{aq}) + 2\text{Cr}^{3+}(\text{aq}) + 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$

**Sol.**

**Q.4** Determine the standard reduction potential for the half reaction:



$$E_{\text{Cell}}^0 = -0.15 \text{ V} \quad \text{Pt}^{2+} + 2\text{e}^- \rightarrow \text{Pt} \quad E^0 = 1.20 \text{ V}$$

**Sol.**

**Q.5** Is 1.0 M  $\text{H}^+$  solution under  $\text{H}_2\text{SO}_4$  at 1.0 atm capable of oxidising silver metal in the presence of 1.0 M  $\text{Ag}^+$  ion ?

$$E_{\text{Ag}^+|\text{Ag}}^0 = 0.80 \text{ V}, \quad E_{\text{H}^+|\text{H}_2(\text{Pt})}^0 = 0.0 \text{ V}$$

**Sol.**

## Electrode potential and standard electrode potential :

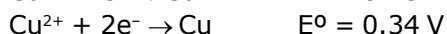
**Q.3** For the cell reaction  $2\text{Ce}^{4+} + \text{Co} \rightarrow 2\text{Ce}^{3+} + \text{Co}^{2+}$

$E_{\text{cell}}^0$  is 1.89 V. If  $E_{\text{Co}^{2+}|\text{Co}}^0$  is - 0.28 V, what is

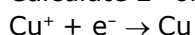
the value of  $E_{\text{Ce}^{4+}|\text{Ce}^{3+}}^0$  ?



**Q.6** If for the half cell reactions



Calculate  $E^\circ$  of the half cell reaction



also predict whether  $\text{Cu}^+$  undergoes disproportionation or not.

**Sol.**

**Q.7** If  $E_{\text{Fe}^{2+}|\text{Fe}}^0 = -0.44 \text{ V}$ ,  $E_{\text{Fe}^{3+}|\text{Fe}^{2+}}^0 = 0.77$ . Calculate  $E_{\text{Fe}^{3+}|\text{Fe}}^0$ .

**Sol.**

**Q.8** Calculate the EMF of a Daniel cell when the concentration of  $\text{ZnSO}_4$  and  $\text{CuSO}_4$  are 0.001 M and 0.1 M respectively. The standard potential of the cell is 1.1 V.

**Sol.**

**Q.9** For a cell  $\text{Mg(s)}|\text{Mg}^{2+}(\text{aq})||\text{Ag}^+(\text{aq})|\text{Ag}$ , Calculate the equilibrium constant at 25°C. Also find the maximum work per mole Ag that can be obtained by operating the cell.

$$E^\circ(\text{Mg}^{2+}/\text{Mg}) = -2.37 \text{ V}, E^\circ(\text{Ag}^+/\text{Ag}) = 0.8 \text{ V}$$

**Sol.**

**Q.10** The EMF of the cell  $\text{M}|\text{M}^{n+}(0.02\text{M})||\text{H}^+(1\text{M})|\text{H}_2(\text{g})$  (1 atm), Pt at 25°C is 0.81 V. Calculate the valency of the metal if the standard oxidation of the metal is 0.76 V.

**Sol.**

**Q.11** Equinormal Solutions of two weak acids,  $\text{HA}(\text{p}K_a = 3)$  and  $\text{HB}(\text{p}K_a = 5)$  are each placed in contact with equal pressure of hydrogen electrode at 25°C. When a cell is constructed by interconnecting them through a salt bridge, find the emf of the cell.

**Sol.**

**Q.12** Calculate  $E^0$  and  $E$  for the cell  $\text{Sn}|\text{Sn}^{2+}(1\text{M})||\text{Pb}^{2+}(10^{-3}\text{M})|\text{Pb}$ ,  $E^0(\text{Sn}^{2+}|\text{Sn}) = -0.14\text{ V}$ ,  $E^0(\text{Pb}^{2+}|\text{Pb}) = -0.13\text{ V}$ . Is cell representation is correct ?

**Sol.**

**Q.13** At what concentration of  $\text{Cu}^{2+}$  in a solution of  $\text{CuSO}_4$  will the electrode potential be zero at  $25^\circ\text{C}$ ?

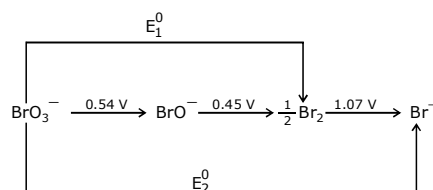
Given :  $E^0(\text{Cu}|\text{Cu}^{2+}) = -0.34\text{ V}$ .

**Sol.**

**Q.14** A zinc electrode is placed in a  $0.1\text{ M}$  solution at  $25^\circ\text{C}$ . Assuming that the salt is 20% dissociated at this dilutions calculate the electrode potential.  $E^0(\text{Zn}^{2+}|\text{Zn}) = -0.76\text{ V}$ .

**Sol.**

**Q.15** From the standard potentials shown in the following diagram, calculate the potentials  $E_1^0$  and  $E_2^0$ .



**Sol.**

#### CONCENTRATION CELLS :

**Q.16** Calculate the EMF of the following cell  $\text{Zn}|\text{Zn}^{2+}(0.01\text{ M})||\text{Zn}^{2+}(0.1\text{ M})|\text{Zn}$  at  $298\text{ K}$ .

**Sol.**

**Q.17** Calculate the EMF of the cell,  $\text{Zn} - \text{Hg}(c_1\text{M})|\text{Zn}^{2+}(\text{aq})|\text{Hg} - \text{Zn}(c_2\text{M})$  at  $25^\circ\text{C}$ , if the concentrations of the zinc amalgam are ;  $c_1 = 10\text{g}$  per  $100\text{ g}$  of mercury and  $c_2 = 1\text{ g}$  per  $100\text{ g}$  of mercury.

**Q.20** Calculate the equilibrium constant for the reaction  $\text{Fe} + \text{CuSO}_4 \rightleftharpoons \text{FeSO}_4 + \text{Cu}$  at  $25^\circ\text{C}$ .  
Given  $E^\circ(\text{Fe}/\text{Fe}^{2+}) = 0.44 \text{ V}$ ,  $E^\circ(\text{Cu}/\text{Cu}^{2+}) = -0.337 \text{ V}$ .

**Q.18** Calculate pH using the following cell:

**Sol.**

**Q.21** The standard reduction potential at 25°C for the reduction of water

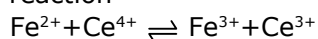
$2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$  is  $-0.8277$  volt.  
Calculate the equilibrium constant for the reaction

$$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \text{ at } 25^\circ\text{C}.$$

**Sol.**

**EQUILIBRIUM CONSTANT :**

**Q.19** Calculate the equilibrium constant for the reaction



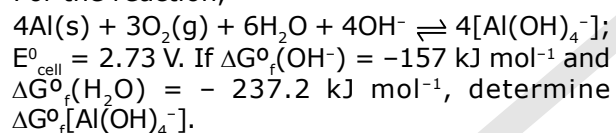
[given :  $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 = 1.44 \text{ V}$ ;  $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.68 \text{ V}$ ]

**Sol.**

**Q.22** At 25°C the value of K for the equilibrium  $\text{Fe}^{3+} + \text{Ag} \rightleftharpoons \text{Fe}^{2+} + \text{Ag}^+$  is 0.531 mol/litre. The standard electrode potential for  $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$  is 0.799 V. What is the standard potential for  $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$ ?

Sol.

Sol.

**Q.23** For the reaction,

Sol.

**Q.25** How many faradays of electricity are involved in each of the case

- (a) 0.25 mole  $\text{Al}^{3+}$  is converted to Al .  
 (b) 27.6 gm of  $\text{SO}_3$  is converted to  $\text{SO}_3^{2-}$   
 (c) The  $\text{Cu}^{2+}$  in 1100 ml of 0.5 M  $\text{Cu}^{2+}$  is converted to Cu.

Sol.

**ELECTROLYTIC CELL****Q.24** Calculate the no. of electrons lost or gained during electrolysis of

- (A) 3.55 gm of  $\text{Cl}^-$  ions  
 (B) 1 gm  $\text{Cu}^{2+}$  ions  
 (C) 2.7 gm of  $\text{Al}^{3+}$  ions

**Q.26** 0.5 mole of electron is passed through two electrolytic cells in series. One contains silver ions, and the other zinc ions. Assume that only cathode reaction in each cell is the reduction of the ion to the metal. How many gm of each metals will be deposited.

Sol.

Sol.

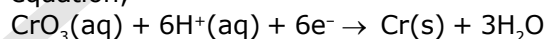
**Q.27** The electrosynthesis of  $\text{MnO}_2$  is carried out from a solution of  $\text{MnSO}_4$  in  $\text{H}_2\text{SO}_4(\text{aq})$ . If a current of 25.5 ampre is used with a current efficiency of 85% how long would it take to produce 1 kg of  $\text{MnO}_2$ ?

Sol.

**Q.29** Assume 96500 C as one unit of electricity. If cost of electricity of producing x gm Al is Rs x, what is the cost of electricity of producing x gm Mg?

Sol.

**Q.30** Chromium metal can be plated out from an acidic solution containing  $\text{CrO}_3$  according t following equation;



Calculate:

- (i) How many grams of chromium will be plated out by 24000 coulombs and
- (ii) How long will it take to plate out 1.5 gm of chromium by using 12.5 ampere current

Sol.

**Q.28** If 0.224 litre of  $\text{H}_2$  gas is formed at the cathode, how much  $\text{O}_2$  gas is formed at the anode under identical condition?

**Q.31** Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 percent. If the potential drop across the cell is 3.0 volts, how much energy will be consumed?

**Sol.**

**Sol.**

**Q.32** How long a current of 2A has to be passed through a solution of  $\text{AgNO}_3$  to coat a metal surface of  $80 \text{ cm}^2$  with  $5 \mu\text{m}$  thick layer? Density of silver =  $10.8 \text{ g/cm}^3$ .

**Sol.**

**Q.34** 10g solution of  $\text{CuSO}_4$  is electrolyzed using 0.01F of electricity. Calculate :

(a) The weight of resulting solution (b) Equivalents of acid or alkali in the solution

**Sol.**

**Q.33** A metal is known to form fluoride  $\text{MF}_2$ . When 10A of electricity is passed through a molten salt for 330 sec., 1.95 g of metal is deposited. Find the atomic weight of M. What will be the quantity of electricity required to deposit the same mass of Cu from  $\text{CuSO}_4$ ?

**Q.35** Cadmium amalgam is prepared by electrolysis of a solution of  $\text{CdCl}_2$  using a mercury cathode. How long should a current of 5A be passed in order to prepare 12% Cd-Hg amalgam on a cathode of 2 gm Hg ( $\text{Cd} = 112.4$ )

**Sol.**

**Q.37** A solution of  $\text{Ni}(\text{NO}_3)_2$  is electrolysed between platinum electrodes using a current of 5 ampere for 20 mintue. What mass of Ni is deposited at the cathode ?

**Sol.**

**Q.36** After electrolysis of NaCl solution with inert electrodes for a certain period of time. 600 mL of the solution was left. Which was found to be 1N in NaOH. During the same time, 31.75 g of Cu was deposited in the copper voltameter in series with the electrolytic cell. calculate the percentage yield of NaOH obtained, if the yield of  $\text{CuSO}_4$  cell is 100%.

**Sol.**

**Q.38** A current of 3.7 A is passed for 6 hrs. between Ni electrodes in 0.5 L of 2M solution of  $\text{Ni}(\text{NO}_3)_2$ . What will be the molarity of solution at the end of electrolysis?

**Sol.**

**CONDUCTANCE****Conductivities and cell constant:**

**Q.39** The resistance of a conductivity cell filled with 0.01 N solution of NaCl is 210 ohm at 18°C. Calculate the equivalent conductivity of the solution. The cell constant of the conductivity cell is  $0.88 \text{ cm}^{-1}$ .

**Sol.**

**Sol.**

**Q.42** For 0.01 N KCl, the resistivity 709.22 ohm cm. Calculate the conductivity and equivalent conductance.

**Sol.**

**Q.40** The molar conductivity of 0.1 M  $\text{CH}_3\text{COOH}$  solution is  $4.6 \text{ S cm}^2 \text{ mole}^{-1}$ . What is the specific conductivity and resistivity of the solution?

**Sol.**

**Q.43** A solution containing 2.08 g of anhydrous barium chloride is 400 CC of water has a specific conductivity  $0.0058 \text{ ohm}^{-1} \text{ cm}^{-1}$ . What are molar and equivalent conductivities of this solution.

**Sol.**

**Q.41** The conductivity of pure water in a conductivity cell with electrodes of cross sectional area  $4 \text{ cm}^2$  and 2 cm apart is  $8 \times 10^{-7} \text{ S cm}^{-1}$ .

(i) What is resistance of conductivity cell ?

(ii) What current would flow through the cell under an applied potential difference of 1 volt?



**Application of Kohlrausch's law :**

**Q.44** For the strong electrolytes NaOH, NaCl and BaCl<sub>2</sub> the molar ionic conductivities at infinite dilution are  $248.1 \times 10^{-4}$ ,  $126.5 \times 10^{-4}$  and  $280.0 \times 10^{-4}$  mho cm<sup>2</sup> mol<sup>-1</sup> respectively. Calculate the molar conductivity of Ba(OH)<sub>2</sub> at infinite dilution.

**Sol.**

**Q.45** Equivalent conductance of 0.01 N Na<sub>2</sub>SO<sub>4</sub> solution is 112.4 ohm<sup>-1</sup> cm<sup>2</sup> eq<sup>-1</sup>. The equivalent conductance at infinite dilution is 129.9 ohm<sup>-1</sup> cm<sup>2</sup> eq<sup>-1</sup>. What is the degree of dissociation in 0.01 N Na<sub>2</sub>SO<sub>4</sub> solution

**Sol.**

**Q.46** The value of  $\Lambda_m^\infty$  for HCl, NaCl and CH<sub>3</sub>CO<sub>2</sub>Na are 426.1, 126.5 and 91 S cm<sup>2</sup> mol<sup>-1</sup> respectively.

Calculate the value of  $\Lambda_m^\infty$  for acetic acid. If the equivalent conductivity of the given acetic acid is 48.15 at 25°C, calculate its degree of dissociation.

**Sol.**

**Q.47** Specific conductance of saturated solution of AgBr is  $8.486 \times 10^{-7}$  ohm<sup>-1</sup> cm<sup>-1</sup> at 25°C. Specific conductance of pure water at 25°C is  $0.75 \times 10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup>.  $\Lambda_m^\infty$  for KBr, AgNO<sub>3</sub> and KNO<sub>3</sub> are 137.4, 133, 131 (S cm<sup>2</sup> mol<sup>-1</sup>) respectively. Calculate the solubility of AgBr in gm/litre.

**Sol.**

**Q.48** Saturated solution of AgCl at 25°C has specific conductance of  $1.12 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The  $\lambda_{\infty} \text{Ag}^{+}$  and  $\lambda_{\infty} \text{Cl}^{-}$  are 54.3 and  $65.5 \text{ ohm}^{-1} \text{ cm}^2 / \text{equi.}$  respectively. Calculate the solubility product of AgCl at 25°C.

**Sol.**

**Q.49** Hydrofluoric acid is weak acid. At 25°C, the molar conductivity of 0.002 M HF is  $176.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ . If its  $\Lambda_m^{\infty} = 405.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ , calculate its degree of dissociation and equilibrium constant at the given concentration.

**Sol.**

**Q.50** At 25°C,  $\lambda_{\infty}(\text{H}^{+}) = 3.4982 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$  and  $\lambda_{\infty}(\text{OH}^{-}) = 1.98 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$ .

Given : Sp. conductance =  $5.7 \times 10^{-6} \text{ Sm}^{-1}$  for  $\text{H}_2\text{O}$ , determine pH and  $K_w$ .

**Sol.**

**51.** The standard reduction potential values,  $E^{\circ}(\text{Bi}^{3+}|\text{Bi})$  and  $E^{\circ}(\text{Cu}^{2+}|\text{Cu})$  are 0.226V and 0.344 V respectively. A mixture of salts of bismuth and copper at unit concentration each is electrolysed at 25°C. to what value can  $[\text{Cu}^{2+}]$  be brought down before bismuth starts to deposit, in electrolysis.

**Sol.**

**52.** The cell  $\text{Pt}, \text{H}_2(1 \text{ atm})|\text{H}^+(\text{pH}=x)||\text{Normal calomel Electrode}$  has an EMF of 0.67V at 25°C. Calculate the pH of the solution. The oxidation potential of the calomel electrode on hydrogen scale is -0.28 V.

**Sol.**

**53.** Voltage of the cell  $\text{Pt}, \text{H}_2(1 \text{ atm})|\text{HOCN}(1.3 \times 10^{-3} \text{ M})||\text{Ag}^+(0.8 \text{ M})|\text{Ag(s)}$  is 0.982 V. Calculate the  $K_a$  for HOCN. Neglect  $[\text{H}^+]$  because of oxidation of  $\text{H}_2(\text{g})$ .  $\text{Ag}^+ + \text{e} \rightarrow \text{Ag(s)} = 0.8 \text{ V}$ .

**Sol.**

**54.** Calculate the potential of an indicator electrode versus the standard hydrogen electrode, which originally contained 0.1 M  $\text{MnO}_4^-$  and 0.8 M  $\text{H}^+$  and which was treated with 90% of the  $\text{Fe}^{2+}$  necessary to reduce all the  $\text{MnO}_4^-$  to  $\text{Mn}^{+2}$ .

$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}, E^\circ = 1.51 \text{ V}$

**Sol.**

**55.** Calculate the emf of the cell

$\text{Pt}, \text{H}_2(1.0 \text{ atm})|\text{CH}_3\text{COOH}(0.1 \text{ M})||\text{NH}_3(\text{aq}, 0.01 \text{ M})|\text{H}_2(1.0 \text{ atm}), \text{Pt}$

$K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}, K_b(\text{NH}_3) = 1.8 \times 10^{-5}$

**Sol.**

**56.** The Edison storage cell is represented as  $\text{Fe(s)}|\text{FeO(s)}|\text{KOH(aq)}|\text{Ni}_2\text{O}_3(\text{s})|\text{Ni(s)}$ . The half-cell reaction are

$\text{Ni}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\ell) + 2\text{e}^- \rightleftharpoons 2\text{NiO(s)} + 2\text{OH}^-$   
 $E^\circ = +0.40 \text{ V}$

$\text{FeO(s)} + \text{H}_2\text{O}(\ell) + 2\text{e}^- \rightleftharpoons \text{Fe(s)} + 2\text{OH}^- \quad E^\circ = -0.87 \text{ V}$

(i) What is the cell reaction?

(ii) What is the cell e.m.f. ? How does it depend on the concentration of KOH?

(iii) What is the maximum amount of electrical energy that can be obtained from one mole of  $\text{Ni}_2\text{O}_3$ ?

**Sol.**

**57.** The standard reduction potential for  $\text{Cu}^{2+}/\text{Cu}$  is 0.34 V. Calculate the reduction potential at pH = 14 for the above couple.  $K_{\text{sp}}$  of  $\text{Cu}(\text{OH})_2$  is  $1 \times 10^{-19}$ .

**Sol.**

**58.** Determine the of hydrolysis and hydrolysis constant of aniline hydrochloride in M/32 solution of salt at 298 K from the following cell data at 298 K.  $\text{Pt}|\text{H}_2(1 \text{ atm})|\text{H}^+(1\text{M})||\text{M}/32 \text{ C}_6\text{H}_5\text{NH}_3\text{Cl}|\text{H}_2(1 \text{ atm})|\text{Pt}$ ;  $E_{\text{cell}} = -0.188\text{V}$ .

**Sol.**

**59.** The emf of the cell,  $\text{Pt}|\text{H}_2(1 \text{ atm}), |\text{H}^+(0.1 \text{ M}, 30 \text{ ml})||\text{Ag}^+(0.8 \text{ M})|\text{Ag}$  is 0.9 V. Calculate the emf when 40 ml of 0.05 M NaOH is added to the anodic compartment.

**Sol.**

**60.** The emf of the cell  $\text{Ag}|\text{AgI}|\text{KI}(0.05\text{M})||\text{AgNO}_3(0.05\text{M})|\text{Ag}$  is 0.788V. Calculate the solubility product of AgI.

**Sol.**

**61.** Consider the cell  $\text{Ag}|\text{AgBr(s)}|\text{Br}||\text{AgCl(s)}, \text{Ag}|\text{Cl}^-$  at  $25^\circ\text{C}$ . The solubility product constants of AgBr & AgCl are respectively  $5 \times 10^{-13}$  &  $1 \times 10^{-10}$ . For what ratio of the concentrations of  $\text{Br}^-$  &  $\text{Cl}^-$  ions would the emf of the cell be zero?

**Sol.**

**62.** The  $pK_{sp}$  of AgI is 16.07. If the  $E^\circ$  value for  $Ag^+|Ag$  is 0.7991 V. Find the  $E^\circ$  for the half cell reaction  $AgI(s) + e^- \rightarrow Ag + I^-$

**Sol.**

**63.** For the galvanic cell:  
 $Ag|AgCl(s)|KCl(0.2M)||KBr(0.001 M)|AgBr(s)|Ag$ ,  
 Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25°C.  
 $[K_{sp}(AgCl) = 2.8 \times 10^{-10}; K_{sp}(AgBr) = 3.3 \times 10^{-13}]$

**Sol.**

**64.** Given,  $E^\circ = -0.268$  V for the  $Cl^-|PbCl_2|Pb$  couple and  $-0.126$  V for the  $Pb^{2+}|Pb$  couple, determine  $K_{sp}$  for  $PbCl_2$  at 25°C?

**Sol.**

**65.** Calculate the voltage,  $E$ , of the cell at 25°C  
 $Mn(s) | Mn(OH)_2(s) | Mn^{2+}(x M), OH^-(1.00 \times 10^{-4} M) || Cu^{2+}(0.675 M) | Cu(s)$  given that  $K_{sp} = 1.9 \times 10^{-13}$  for  $Mn(OH)_2(s)$ ,  $E^\circ(Mn^{2+}/Mn) = -1.18$  V.

**Sol.**

**66.** Calculate the voltage,  $E$ , of the cell  
 $Ag(s) | AgIO_3(s) | Ag^+(x M), HIO_3(0.300M) || Zn^{2+}(0.175 M) | Zn(s)$  if  $K_{sp} = 3.02 \times 10^{-8}$  for  $AgIO_3(s)$  and  $K_a = 0.162$  for  $HIO_3$ .

**Sol.**

**67.** Estimate the cell potential of a Daniel cell having 1 M  $Zn^{++}$  & originally having 1M  $Cu^{++}$  after sufficient  $NH_3$  has been added to the cathode compartment to make  $NH_3$  concentration 2M.  
 $K_f$  for  $[Cu(NH_3)_4]^{2+} = 1 \times 10^{12}$ ,  $E^\circ$  for the reaction,  $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$  is 1.1 V.

**Sol.**

**68.** The overall formation constant for the reaction of 6 mol of  $\text{CN}^-$  with cobalt (II) is  $1 \times 10^{19}$ . The standard reduction potential for the reaction.

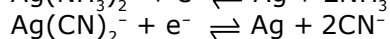
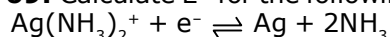
$[\text{Co}(\text{CN})_6]^{3-} + \text{e}^- \rightarrow \text{Co}(\text{CN})_6^{4-}$  is  $-0.83 \text{ V}$ . Calculate the formation constant of  $[\text{Co}(\text{CN})_6]^{3+}$

Given  $\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$ ;  $E^\circ = 1.82 \text{ V}$

**Sol.**

**Sol.**

**69.** Calculate  $E^\circ$  for the following reactions at 298 K,



Given :  $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.7991 \text{ V}$ ,  $K_{\text{Ins}}[\text{Ag}(\text{NH}_3)_2^+] = 6.02 \times 10^{-8}$  and  $K_{\text{Ins}}[\text{Ag}(\text{CN})_2^-] = 1.995 \times 10^{-19}$

**Sol.**

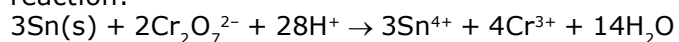
**71.** Calculate the equilibrium concentrations of all ions in an ideal solution prepared by mixing 25.00 mL of 0.100 M  $\text{TI}^+$  with 25.00 mL of 0.200 M  $\text{Co}^{3+}$   
 $E^\circ(\text{TI}^+/\text{TI}^{3+}) = -1.25 \text{ V}$ ;  $E^\circ(\text{Co}^{3+}/\text{Co}^{2+}) = 1.84 \text{ V}$

**Sol.**

**72.** One of the methods of preparation of perdisulphuric acid,  $\text{H}_2\text{S}_2\text{O}_8$ , involve electrolytic oxidation of  $\text{H}_2\text{SO}_4$  at anode ( $2\text{H}_2\text{SO}_4 \rightarrow 2\text{H}_2\text{S}_2\text{O}_8 + 2\text{H}^+ + 2\text{e}^-$ ) with oxygen and hydrogen as by-products. In such an electrolysis, 9.722 L of  $\text{H}_2$  and 2.35 L of  $\text{O}_2$  were generated at STP. What is the weight of  $\text{H}_2\text{S}_2\text{O}_8$  formed?

**Sol.**

**70.** Calculate the equilibrium constant for the reaction:



$E^\circ$  for  $\text{Sn}/\text{Sn}^{2+} = 0.136 \text{ V}$   $E^\circ$  for  $\text{Sn}^{2+}/\text{Sn}^{4+} = -0.154 \text{ V}$

$E^\circ$  for  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+} = 1.33 \text{ V}$

**73.** A current of 3 amp was passed for 2 hour through a solution of  $\text{CuSO}_4$ , 3g of  $\text{Cu}^{2+}$  ions were deposited as Cu at cathode. Calculate percentage current efficiency of the process.

**Sol.**

**74.** An acidic solution of  $\text{Cu}^{2+}$  salt containing 0.4 g of  $\text{Cu}^{2+}$  is electrolyzed until all the copper is deposited. The electrolysis is continued for sever more minutes with the volume of solution kept at 100 ml and the current at 1.2 amp. Calculate the volume of gases evolved at NTP during the entire electrolysis.

**Sol.**

**75.** In the refining of silver by electrolytic method what will be the weight of 100 gm Ag anode if 5 ampere current is passed for 2 hours? Purity of silver is 95% by weight.

**Sol.**

**76.** Dal lake has water  $8.2 \times 10^{12}$  litre approximately. A power reactor produces electricity at the rate of  $1.5 \times 10^6$  coulomb per second at an appropriate voltage. How many years would it take to electrolyse the lake?

**Sol.**

**77.** A lead storage cell is discharged which causes the  $\text{H}_2\text{SO}_4$  electrolyte to change from a concentration of 34.6 % by weight (density  $1.261 \text{ g ml}^{-1}$  at  $25^\circ\text{C}$ ) to 27% by weight. The original volume of electrolyte is one litre. Calculate the total charge released at anode of the battery. Note that the water is produced by the cell reaction as  $\text{H}_2\text{SO}_4$  is used up. Over all reaction is  
$$\text{Pb(s)} + \text{PbO}_2\text{(s)} + 2\text{H}_2\text{SO}_4\text{(l)} \rightarrow 2\text{PbSO}_4\text{(s)} + 2\text{H}_2\text{O(l)}$$

**Sol.**

**78.** Determine at 298 for Cell  
 $\text{Pt} | \text{Q}, \text{QH}_2\text{H}^+ || 1\text{M KCl} | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}(\text{l}) | \text{Pt}$   
 (a) It's emf when  $\text{pH} = 5.0$   
 (b) the  $\text{pH}$  when  $E_{\text{cell}} = 0$   
 (c) the positive electrode when  $\text{pH} = 7.5$   
 given  $E_{\text{RP(RHS)}}^0 = 0.28$ ,  $E_{\text{RP(LHS)}}^0 = 0.699$

**Sol.**

**79.** Calculate the cell potential of a cell having reaction:  $\text{Ag}_2\text{S} + 2\text{e}^- \rightleftharpoons 2\text{Ag} + \text{S}^{2-}$  in a solution buffered at  $\text{pH} = 3$  and which is also saturated with  $0.1\text{ M H}_2\text{S}$ .

For  $\text{H}_2\text{S}$  :  $K_1 = 10^{-8}$  and  $K_2 = 1.1 \times 10^{-13}$ ,  $K_{\text{sp}}(\text{Ag}_2\text{S}) = 2 \times 10^{-49}$ ,  $E_{\text{Ag}^+/\text{Ag}}^0 = 0.8$ .

**Sol.**

**80.** The equivalent conductance of  $0.10\text{ N}$  solution of  $\text{MgCl}_2$  is  $97.1\text{ mho cm}^2 \text{ eq}^{-1}$  at  $25^\circ\text{C}$ . a cell with electrode that are  $1.5\text{ cm}^2$  in surface area and  $0.5\text{ cm}$  apart is filled with  $0.1\text{ N MgCl}_2$  solution. How much current will flow when potential difference between the electrodes is  $5\text{ volt}$ .

**Sol.**

**81.** A dilute aqueous solution of  $\text{KCl}$  was placed between two electrodes  $10\text{ cm}$  apart, across which a potential of  $6\text{ volt}$  was applied. How far would the  $\text{K}^+$  ion move in  $2\text{ hours}$  at  $25^\circ\text{C}$ ? Ionic conductance of  $\text{K}^+$  ion at infinite dilution to  $25^\circ\text{C}$  is  $73.52\text{ ohm}^{-1}\text{ cm}^2 \text{ mole}^{-1}$ ?

**Sol.**



**82.** When a solution of specific conductance  $1.342 \text{ ohm}^{-1} \text{ metre}^{-1}$  was placed in a conductivity cell with parallel electrodes, the resistance was found to be  $170.5 \text{ ohm}$ . Area of electrodes is  $1.86 \times 10^{-6} \text{ cm}^2$ . Calculate separation of electrodes.

**Sol.**

**83.** The specific conductance at  $25^\circ\text{C}$  of a saturated solution  $\text{SrSO}_4$  is  $1.482 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$  while that of water used is  $1.5 \times 10^{-6} \text{ mho cm}^{-1}$ . Determine at  $25^\circ\text{C}$  the solubility in gm per litre of  $\text{SrSO}_4$  in water. Molar ionic conductance of  $\text{Sr}^{2+}$  and  $\text{SO}_4^{2-}$  ions at infinite dilution are  $59.46$  and  $79.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  respectively. [ $\text{Sr} = 87.6$ ,  $\text{S} = 32$ ,  $\text{O} = 16$ ]

**Sol.**

**84.** Calculate the solubility and solubility product of  $\text{Co}_2[\text{Fe}(\text{CN})_6]$  in water at  $25^\circ\text{C}$  from the following data:

Conductivity of a saturated solution of  $\text{Co}_2[\text{Fe}(\text{CN})_6]$  is  $2.06 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$  and that of water used  $4.1 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$ . The ionic molar conductivities of  $\text{Co}^{2+}$  and  $\text{Fe}(\text{CN})_6^{4-}$  are  $86.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  and  $444.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

**Sol.**

**85.** In two vessels each containing  $500 \text{ ml}$  water,  $0.5 \text{ m mol}$  of aniline ( $K_b = 10^{-9}$ ) and  $25 \text{ mmol}$  of  $\text{HCl}$  are added separately. Two hydrogen electrodes are constructed using these solutions. Calculate the emf of cell made by connecting them appropriately.

**Sol.**

## Exercise - IV

## PREVIOUS YEAR QUESTIONS

## LEVEL - I

## JEE MAIN

1. For the following cell with hydrogen electrodes at two different pressure  $p_1$  and  $p_2$   
 $\text{Pt}(\text{H}_2)|\text{H}^+(\text{aq.})|\text{Pt}(\text{H}_2)|\text{H}^+(\text{aq.})$  emf is given by –  $p_1 \quad p_2$  [AIEEE-2002]

- (A)  $\frac{RT}{F} \log_e \frac{p_1}{p_2}$  (B)  $\frac{RT}{2F} \log_e \frac{p_1}{p_2}$   
 (C)  $\frac{RT}{F} \log_e \frac{p_2}{p_1}$  (D)  $\frac{RT}{2F} \log_e \frac{p_2}{p_1}$

Sol.

2. Which of the following reaction is possible at anode ? [AIEEE-2002]  
 (A)  $\text{F}_2 + 2\text{e}^- \longrightarrow 2\text{F}^-$   
 (B)  $2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^- \longrightarrow \text{H}_2\text{O}$   
 (C)  $2\text{Cr}^{3+} + 7\text{H}_2\text{O} \longrightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^-$   
 (D)  $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{e}^-$

Sol.

3. Refining of impure copper with zinc impurity is to be done by electrolysis using electrodes as – [AIEEE-2002]

- |                 |               |
|-----------------|---------------|
| Cathode         | Anode         |
| (A) Pure copper | Pure zinc     |
| (B) Pure zinc   | Pure copper   |
| (C) Pure copper | Impure copper |
| (D) Pure zinc   | Impure zinc   |

Sol.

4. For a cell given below  
 $\text{Ag} | \text{Ag}^+ || \text{Cu}^{2+} | \text{Cu}$   
 — +  
 $\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}, \quad E^\circ = x$   
 $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}, \quad E^\circ = y$   
 $E^\circ_{\text{cell}}$  is – [AIEEE-2002]  
 (A)  $x + 2y$  (B)  $2x + y$   
 (C)  $y - x$  (D)  $y - 2x$

Sol.

5. For a cell reaction involving a two-electron change the standard e.m.f. of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25°C will be – [AIEEE-2003]  
 (A) 10 (B)  $1 \times 10^{10}$   
 (C)  $1 \times 10^{-10}$  (D)  $29.5 \times 10^{-2}$

Sol.

6. Standard reduction electrode potentials of three metals A, B and C are respectively +0.5 V, – 3.0V and – 1.2 V. The reducing powers of these metals are – [AIEEE-2003]  
 (A)  $C > B > A$  (B)  $A > C > B$   
 (C)  $B > C > A$  (D)  $A > B > C$

Sol.

7. For the redox reaction :  
 $\text{Zn (s)} + \text{Cu}^{2+} (0.1\text{M}) \longrightarrow \text{Zn}^{2+} (1\text{M}) + \text{Cu (s)}$   
 taking place in a cell,  $E^\circ_{\text{cell}}$  is 1.10 volt.  $E_{\text{cell}}$   
 for the cell will be  $\left(2.303 \frac{RT}{F} = 0.0591\right)$   
**[AIEEE-2003]**  
 (A) 1.07 volt (B) 0.82 volt  
 (C) 2.14 volt (D) 1.8 volt

Sol.

8. When during electrolysis of a solution of  $\text{AgNO}_3$ , 9650 coulombs of charge pass through the electroplating bath, the mass of silver deposited on the cathode will be –  
**[AIEEE-2003]**  
 (A) 21.6 g (B) 108 g  
 (C) 1.08 g (D) 10.8 g

Sol.

9. Consider the following  $E^\circ$  values  
 $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.77 \text{ V}$  **[AIEEE-2004]**  
 $E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.14 \text{ V}$   
 Under standard conditions the potential for the reaction  
 $\text{Sn}_{(\text{s})} + 2\text{Fe}^{3+}_{(\text{aq})} \rightarrow 2\text{Fe}^{2+}_{(\text{aq})} + \text{Sn}^{2+}_{(\text{aq})}$  is  
 (A) 1.68 V (B) 1.40 V  
 (C) 0.91 V (D) 0.63 V

Sol.

10. The standard e.m.f. of a cell, involving one electron change is found to be 0.591 V at  $25^\circ\text{C}$ . The equilibrium constant of the reaction is ( $F = 96500 \text{ C mol}^{-1}$ ;  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ )  
**[AIEEE-2004]**  
 (A)  $1.0 \times 10^1$  (B)  $1.0 \times 10^5$   
 (C)  $1.0 \times 10^{10}$  (D)  $1.0 \times 10^{30}$

Sol.

11. The limiting molar conductivities  $\wedge^\circ$  for NaCl, KBr and KCl are 126, 152 and  $150 \text{ S cm}^2 \text{ mol}^{-1}$  respectively. The  $\wedge^\circ$  for NaBr is –  
**[AIEEE-2004]**  
 (A)  $128 \text{ S cm}^2 \text{ mol}^{-1}$  (B)  $176 \text{ S cm}^2 \text{ mol}^{-1}$   
 (C)  $278 \text{ S cm}^2 \text{ mol}^{-1}$  (D)  $302 \text{ S cm}^2 \text{ mol}^{-1}$

Sol.

12. In a cell that utilises the reaction  
 $\text{Zn}_{(\text{s})} + 2\text{H}^{+}_{(\text{aq})} \rightleftharpoons \text{Zn}^{2+}_{(\text{aq})} + \text{H}_{2(\text{g})}$  addition of  $\text{H}_2\text{SO}_4$  to cathode compartment, will –  
**[AIEEE-2004]**  
 (A) lower the E and shift equilibrium to the left  
 (B) lower the E and shift equilibrium right  
 (C) increase the E and shift equilibrium to the right  
 (D) increase the E and shift equilibrium to the left

Sol.

- 13.** Aluminium oxide may be electrolysed at  $1000^{\circ}\text{C}$  to furnish aluminium metal (At. Mass = 27 amu ; 1 Faraday = 96,500 Coulombs). The cathode reaction is  $\text{Al}^{3+} + 3\text{e}^{-} \longrightarrow \text{Al}^0$ . To prepare 5.12 kg of aluminium metal by this method would require - **[AIEEE-2005]**
- (A)  $1.83 \times 10^7$  C of electricity  
 (B)  $5.49 \times 10^7$  C of electricity  
 (C)  $5.49 \times 10^1$  C of electricity  
 (D)  $5.49 \times 10^4$  C of electricity

Sol.

**14.**

Electrolyte	KCl	KNO <sub>3</sub>	HCl	NaOAc	NaCl
$\Lambda^{\infty} (\text{S cm}^2 \text{mol}^{-1})$ :	149.9	145.0	426.2	91.0	126.5

Calculate  $\Lambda_{\text{HOAc}}^{\infty}$  using appropriate molar conductance of the electrolytes listed above at infinite dilution in  $\text{H}_2\text{O}$  at  $25^{\circ}\text{C}$  **[AIEEE-2005]**

- (A) 552.7 (B) 517.2  
 (C) 217.5 (D) 390.7

Sol.

- 15.** For a spontaneous reaction the  $\Delta G$ , equilibrium constant (K) and  $E_{\text{cell}}$  will be respectively - **[AIEEE-2005]**

- (A) +ve, > 1, -ve (B) -ve, > 1, +ve  
 (C) -ve, > 1, -ve (D) -ve, < 1, -ve

Sol.

- 16.** Given the data at  $25^{\circ}\text{C}$ ,  
 $\text{Ag} + \text{I}^{-} \rightarrow \text{AgI} + \text{e}^{-}$   $E^{\circ} = 0.152 \text{ V}$   
 $\text{Ag} \rightarrow \text{Ag}^{+} + \text{e}^{-}$   $E^{\circ} = -0.800 \text{ V}$   
 What is the value of  $\log K_{\text{sp}}$  for AgI ?  
 ( $2.303 \text{ RT/F} = 0.059 \text{ V}$ ) **[AIEEE 2006]**
- (A) +8.612 (B) -37.83  
 (C) -16.13 (D) -8.12

Sol.

- 17.** The cell,  $\text{Zn} | \text{Zn}^{2+} (1\text{M}) || \text{Cu}^{2+} (1\text{M}) | \text{Cu}$  ( $E^{\circ}_{\text{cell}} = 1.10 \text{ V}$ ), was allowed to be completely discharged at 298 K. The relative concentration

of  $\text{Zn}^{2+}$  to  $\text{Cu}^{2+}$   $\left( \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)$  is - **[AIEEE 2007]**

- (A) Antilog (24.08) (B) 37.3  
 (C)  $10^{37.3}$  (D)  $9.65 \times 10^4$

Sol.

Sol.

18. The equivalent conductance of two strong electrolytes at infinite dilution in  $H_2O$  (where ions move freely through a solution) at  $25^\circ C$  are given below - **[AIEEE 2007]**

$$\Lambda^\circ_{CH_3COONa} = 91.0 \text{ S cm}^2/\text{equiv}$$

$$\Lambda^\circ_{HCl} = 426.2 \text{ S cm}^2/\text{equiv}$$

What additional information/quantity one needs to calculate  $\Lambda^\circ$  of an aqueous solution of acetic acid ?

- (A)  $\Lambda^\circ$  of NaCl (B)  $\Lambda^\circ$  of  $CH_3COOH$   
(C) The limiting equivalent conductance

$$\text{of } H^+ (\lambda^\circ_{H^+})$$

- (D)  $\Lambda^\circ$  of chloroacetic acid ( $ClCH_2COOH$ )

Sol.

20. The standard reduction potentials for  $Zn^{2+}/Zn$ ,  $Ni^{2+}/Ni$ , and  $Fe^{2+}/Fe$  are  $-0.76$ ,  $-0.23$  and  $-0.44 \text{ V}$  respectively. The reaction  $X + Y^{2+} \rightarrow X^{2+} + Y$  will be spontaneous when -

**[AIEEE 2012]**

- (A)  $X = Ni$ ,  $Y = Zn$  (B)  $X = Fe$ ,  $Y = Zn$   
(C)  $X = Zn$ ,  $Y = Ni$  (D)  $X = Ni$ ,  $Y = Fe$

Sol.

21. Given

$$E^\circ_{Cr^{3+}/Cr} = -0.74V; E^\circ_{MnO_4^-/Mn^{2+}} = 1.51V$$

$$E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33V; E^\circ_{Cl/Cl^-} = 1.36V$$

Based on the data given above, strongest oxidising agent will be **[AIEEE 2013]**

- (A)  $Mn^{2+}$  (B)  $MnO_4^-$   
(C)  $Cl^-$  (D)  $Cr^{3+}$

19. Given  $E^\circ_{Cr^{3+}/Cr} = -0.72 \text{ V}$ ,  $E^\circ_{Fe^{2+}/Fe} = -0.42 \text{ V}$ .  
The potential for the cell  $Cr | Cr^{3+} (0.1 \text{ M}) || Fe^{2+} (0.01 \text{ M}) | Fe$  is - **[AIEEE 2008]**  
(A)  $0.339 \text{ V}$  (B)  $-0.339 \text{ V}$   
(C)  $-0.26 \text{ V}$  (D)  $0.26 \text{ V}$

## LEVEL - II

## JEE ADVANCED

1. Calculate the equilibrium constant for the reaction,  $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$ . The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{I}_3^-/\text{I}^-$  couples. [JEE-1998]

Sol.

Sol.

2. Find the solubility product of a saturated solution of  $\text{Ag}_2\text{CrO}_4$  in water at 298 K if the emf of the cell  $\text{Ag}|\text{Ag}^+(\text{satd. Ag}_2\text{CrO}_4 \text{ soln.})||\text{Ag}^+(0.1 \text{ M})|\text{Ag}$  is 0.164 V at 298 K. [JEE-1998]

Sol.

4. For the electrochemical cell,  $\text{M}|\text{M}^+||\text{X}^-|\text{X}$ ,  $E^\circ(\text{M}^+/\text{M}) = 0.44 \text{ V}$  and  $E^\circ(\text{X}/\text{X}^-) = 0.33 \text{ V}$ . From this data, one can deduce that

- (A)  $\text{M} + \text{X} \rightarrow \text{M}^+ + \text{X}^-$  is the spontaneous reaction  
 (B)  $\text{M}^+ + \text{X}^- \rightarrow \text{M} + \text{X}$  is the spontaneous reaction  
 (C)  $E_{\text{Cell}} = 0.77 \text{ V}$   
 (D)  $E_{\text{Cell}} = -0.77 \text{ V}$  [JEE-2000]

Sol.

3. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y and 1 M Z at 25°C. If the reduction potential of  $\text{Z} > \text{Y} > \text{X}$ , then  
 (A) Y will oxidise X and not Z  
 (B) Y will oxidise Z and X  
 (C) Y will oxidise both X and Z  
 (D) Y will reduce both X and Z [JEE-1999]

5. Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 mintue. It was found that after electrolysis, the absorbance (concentration) of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with. [JEE-2000]

Sol.

6. The following electrochemical cell has been set up  
 $\text{Pt}_{(I)}|\text{Fe}^{3+}, \text{Fe}^{2+}(a=1)||\text{Ce}^{4+}, \text{Ce}^{3+}(a=1)|\text{Pt}_{(II)}$   
 $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.77 \text{ V}$  and  $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 = 1.61 \text{ V}$

If an ammeter is connected between the two platinum electrodes. Predict the direction of flow of current. Will the current increase or decrease with time? [JEE-2000]

Sol.

7. The reaction,  
 $3\text{ClO}^-(\text{aq}) \rightarrow \text{ClO}_3^-(\text{aq}) + 2\text{Cl}^-(\text{aq})$   
is an example of  
(A) Oxidation reaction  
(B) Reduction reaction  
(C) Disproportionation reaction  
(D) Decomposition reaction [JEE-2001]

Sol.

8. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is  
(A) LiCl > NaCl > KCl (B) KCl > NaCl > LiCl  
(C) NaCl > KCl > LiCl (D) LiCl > KCl > NaCl [JEE-2001]

Sol.

9. Saturated solution of  $\text{KNO}_3$  is used to make salt bridge because  
(A) Velocity of  $\text{K}^+$  is greater than that of  $\text{NO}_3^-$   
(B) Velocity of  $\text{NO}_3^-$  is greater than that of  $\text{K}^+$   
(C) Velocities of both  $\text{K}^+$  and  $\text{NO}_3^-$  are nearly the same  
(D)  $\text{KNO}_3$  is highly soluble in water [JEE-2001]

Sol.

- 10.** The standard potential of the following cell is 0.23 V at 15°C & 0.21 V at 35°C  
 $\text{Pt}|\text{H}_2(\text{g})|\text{HCl}(\text{aq})|\text{AgCl}(\text{s})|\text{Ag}(\text{s})$
- Write the cell reaction.
  - Calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$  for the cell reaction by assuming that these quantities remain unchanged in the range 15°C to 35°C.
  - Calculate the solubility of AgCl in water at 25°C. Given standard reduction potential of the  $\text{Ag}^+/\text{Ag}$  couple is 0.80 V at 25°C. **[JEE-2001]**

**Sol.**

- 11.** Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below.
- $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}); E^\circ = 1.51 \text{ V}$
- $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l}); E^\circ = 1.38 \text{ V}$
- $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq}) ; E^\circ = 0.77 \text{ V}$
- $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq}) ; E^\circ = 1.40 \text{ V}$
- Identify the only incorrect statement regarding quantitative estimation of aqueous  $\text{Fe}(\text{NO}_3)_2$
- $\text{MnO}_4^-$  can be used in aqueous HCl
  - $\text{Cr}_2\text{O}_7^{2-}$  can be used in aqueous HCl
  - $\text{MnO}_4^-$  can be used in aqueous  $\text{H}_2\text{SO}_4$
  - $\text{Cr}_2\text{O}_7^{2-}$  can be used in aqueous  $\text{H}_2\text{SO}_4$

**[JEE-2002]**

**Sol.**

- 12.** In the electrolytic cell, flow of electrons is from
- Cathode to anode in solution
  - Cathode to anode through external supply
  - Cathode to anode through internal supply
  - Anode to cathode through internal supply

**[JEE-2003]**

**Sol.**

- 13.** Two students use same stock solution of  $\text{ZnSO}_4$  and a solution of  $\text{CuSO}_4$ . The e.m.f of one cell is 0.03 V higher than the other. The conc. of  $\text{CuSO}_4$  in the cell with higher e.m.f value is 0.5 M. Find out the conc. of  $\text{CuSO}_4$  in the other cell

$$\left( \frac{2.303RT}{F} = 0.06 \right).$$

**[JEE-2003]**

**Sol.**

- 14.**  $\text{Zn}|\text{Zn}^{2+}(\text{a}=0.1\text{M})||\text{Fe}^{2+}(\text{a}=0.01 \text{ M})|\text{Fe}$ . the emf of the above cell is 0.2905 V Equilibrium constant for the cell reaction is

- $10^{0.32/0.0591}$
- $10^{0.32/0.0295}$
- $10^{0.26/0.0295}$
- $e^{0.32/0.295}$

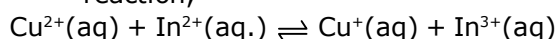
**[JEE-2004]**



Sol.

Sol.

15. Find the equilibrium constant at 298 K for the reaction,



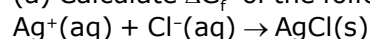
Given that  $E_{\text{Cu}^{2+}/\text{Cu}^+}^0 = 0.15\text{V}$ ,  $E_{\text{In}^{3+}/\text{In}^{2+}}^0 = -0.42\text{V}$ ,

$$E_{\text{In}^{2+}/\text{In}^+}^0 = -0.40\text{V}$$

[JEE-2004]

Sol.

17. (a) Calculate  $\Delta G_f^0$  of the following reaction



given  $\Delta_f G^0(\text{AgCl}) = -109\text{ kJ/mole}$ ,

$\Delta_f G^0(\text{Cl}^-) = -129\text{ kJ/mole}$ ,

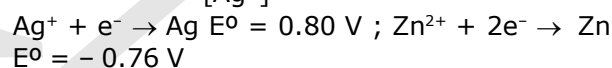
$\Delta_f G^0(\text{Ag}^+) = 77\text{ kJ/mole}$

Represent the above reaction in form of a cell

Calculate  $E^0$  of the cell. Find  $\log_{10} K_{\text{sp}}$  of AgCl

(b)  $6.539 \times 10^{-2}\text{ g}$  of metallic Zn ( $\text{amu} = 65.39$ ) was added to 100 ml of saturated solution of AgCl.

Calculate  $\log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$ , given that

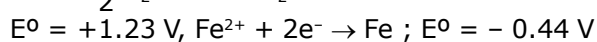
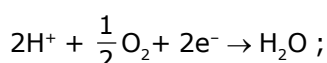


Also find how many moles of Ag will be formed?

[JEE-2005]

Sol.

16. The half cell reactions for rusting of iron are:

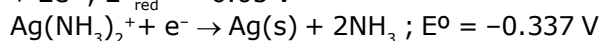
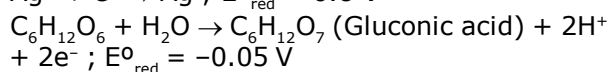
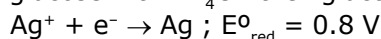


$\Delta G^0$  ( in kJ) for the reaction is : [JEE-2005]

(A) -76    (B) -322    (C) -122    (D) -176

**Question No. 18 to 20 (3 questions)**

Tollen's reagent is used for the detection of aldehyde when a solution of  $\text{AgNO}_3$  is added to glucose with  $\text{NH}_4\text{OH}$  then gluconic acid is formed.



[Use  $2.303 \times \frac{RT}{F} = 0.0592$  and  $\frac{F}{RT} = 38.92$  at

298 K ]

**[JEE-2006]**

- 18.**  $2\text{Ag}^+ + \text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O} \rightarrow 2\text{Ag(s)} + \text{C}_6\text{H}_{12}\text{O}_7 + 2\text{H}^+$   
Find  $\ln K$  of this reaction  
(A) 66.13 (B) 58.38  
(C) 28.30 (D) 46.29

**Sol.**

- 19.** When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much?  
(A)  $E_{\text{oxd}}$  will increase by a factor of 0.65 from  $E_{\text{oxd}}^0$   
(B)  $E_{\text{oxd}}$  will decrease by a factor of 0.65 from  $E_{\text{oxd}}^0$   
(C)  $E_{\text{red}}$  will increase by a factor of 0.65 from  $E_{\text{red}}^0$   
(D)  $E_{\text{red}}$  will decrease by a factor of 0.65 from  $E_{\text{red}}^0$

**Sol.**

- 20.** Ammonia is always added in this reaction. Which of the following must be incorrect ?

- (A)  $\text{NH}_3$  combines with  $\text{Ag}^+$  to form a complex.  
(B)  $\text{Ag}(\text{NH}_3)_2^+$  is a weaker oxidising reagent than  $\text{Ag}^+$   
(C) In absence of  $\text{NH}_3$  silver salt of gluconic acid is formed.  
(D)  $\text{NH}_3$  has affected the standard reduction potential of glucose/ gluconic acid electrode.

**Sol.**

- 21.** We have taken a saturated solution of  $\text{AgBr}$ .  $K_{\text{sp}}$  of  $\text{AgBr}$  is  $12 \times 10^{-14}$ . If  $10^{-7}$  mole of  $\text{AgNO}_3$  are added to 1 litre of this solution find conductivity (specific conductance) of this solution in terms of  $10^{-7} \text{ S m}^{-1} \text{ mole}^{-1}$ . **[JEE-2006]**

[Given :  $\lambda_{(\text{Ag}^+)}^0 = 6 \times 10^{-3} \text{ Sm}^2 \text{ mol}^{-1}$  ;

$\lambda_{(\text{Br}^-)}^0 = 8 \times 10^{-3} \text{ Sm}^2 \text{ mol}^{-1}$  ;  $\lambda_{(\text{NO}_3^-)}^0 = 7 \times 10^{-2} \text{ Sm}^2 \text{ mol}^{-1}$ ]

**Sol.**

**Question No. 22 to 24 (3 questions)**

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately  $6.023 \times 10^{23}$ ) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 molar aqueous solution NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass : Na = 23, Hg = 200, 1 faraday = 96500 coulombs)

[JEE-2007]

22. The total number of moles of chlorine gas evolved is

(A) 0.5 (B) 1.0  
(C) 2.0 (D) 3.0

Sol.

23. If the cathode is a Hg electrode, the maximum weight (g) of amalgam formed from this solution is

(A) 200 (B) 225  
(C) 400 (D) 446

Sol.

24. The total charge (coulombs) required for complete electrolysis is

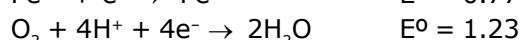
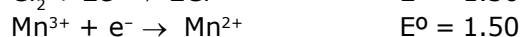
(A) 24125 (B) 48250  
(C) 96500 (D) 193000

Sol.

**Question No. 25 to 26 (2 questions)**

Redox reactions play a pivotal role in chemistry and biology. The values of standard redox potential ( $E^0$ ) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their  $E^0$  (V with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to Questions

[JEE-2007]



25. Among the following, identify the correct statement.

(A) Chloride ion is oxidised by  $\text{O}_2$   
(B)  $\text{Fe}^{2+}$  is oxidised by iodine  
(C) Iodine ion oxidised by chlorine  
(D)  $\text{Mn}^{2+}$  is oxidised by chlorine

Sol.

26. While  $\text{Fe}^{3+}$  is stable,  $\text{Mn}^{3+}$  is not stable in acid solution because

(A)  $\text{O}_2$  oxidises  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$   
(B)  $\text{O}_2$  oxidises both  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  and  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$   
(C)  $\text{Fe}^{3+}$  oxidises  $\text{H}_2\text{O}$  to  $\text{O}_2$   
(D)  $\text{Mn}^{3+}$  oxidises  $\text{H}_2\text{O}$  to  $\text{O}_2$

Sol.

- 27.** Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milli ampere current. The time required to liberate 0.01 mol of  $H_2$  gas at the cathode is (1 Faraday =  $96500\text{ C mol}^{-1}$ )
- (A)  $9.65 \times 10^4\text{ sec}$   
 (B)  $19.3 \times 10^4\text{ sec}$   
 (C)  $28.95 \times 10^4\text{ sec}$   
 (D)  $38.6 \times 10^4\text{ sec}$
- Sol.**

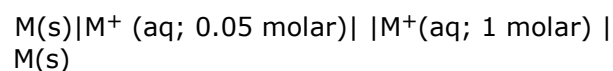
[JEE-2008]

- 28.** For the reaction of  $NO_3^-$  ion in an aqueous solution,  $E^\circ$  is +0.96 V. Values of  $E^\circ$  for some metal ions are given below
- $V^{2+}(\text{aq}) + 2e^- \rightarrow V \quad E^\circ = -1.19\text{ V}$   
 $Fe^{3+}(\text{aq}) + 3e^- \rightarrow Fe \quad E^\circ = -0.04\text{ V}$   
 $Au^{3+}(\text{aq}) + 3e^- \rightarrow Au \quad E^\circ = +1.40\text{ V}$   
 $Hg^{2+}(\text{aq}) + 2e^- \rightarrow Hg \quad E^\circ = +0.86\text{ V}$
- The pair(s) of metal that is(are) oxidised by  $NO_3^-$  in aqueous solution is(are):
- (A) V and Hg  
 (B) Hg and Fe  
 (C) Fe and Au  
 (D) Fe and V
- Sol.**

[JEE-2009]

**Paragraph for Question 30 to 31 [JEE-2010]**

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is:



For the above electrolytic cell the magnitude of the cell potential  $|E_{\text{cell}}| = 70\text{ mV}$ .

- 30.** For the above cell
- (A)  $E_{\text{cell}} < 0$  ;  $\Delta G > 0$   
 (B)  $E_{\text{cell}} > 0$  ;  $\Delta G < 0$   
 (C)  $E_{\text{cell}} < 0$  ;  $\Delta G^\circ > 0$   
 (D)  $E_{\text{cell}} > 0$  ;  $\Delta G^\circ < 0$

**Sol.**

- 29.** Among the following the intensive property is (Properties are )
- (A) molar conductivity (B) electromotive force  
 (C) resistance (D) heat capacity

31. In the 0.05 molar solution of  $M^+$  is replaced by a 0.0025 molar  $M^+$  solution, then the magnitude of the cell potential would be

(A) 35 mV (B) 70 mV  
(C) 140 mV (D) 700 mV

**Sol.**

**Paragraph for Question Nos. 33 and 34**

The electrochemical cell shown below is a concentration cell.

$M | M^{2+}$  (saturated solution of a sparingly soluble salt,  $MX_2$ )  $||$   $M^{2+}$  ( $0.001 \text{ mol dm}^{-3}$ )  $| M$   
The emf of the cell depends on the difference in concentrations of  $M^{2+}$  ions at the two electrodes. The emf of the cell at 298 K is 0.059 V.  
**[IIT-2012]**

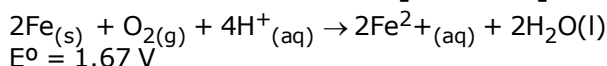
33. The solubility product ( $K_{sp}$ ;  $\text{mol}^3 \text{ dm}^{-9}$ ) of  $MX_2$  at 298 K based on the information available for the given concentration cell is (take  $2.303 \times R \times 298 / F = 0.059 \text{ V}$ )

(A)  $1 \times 10^{-15}$  (B)  $4 \times 10^{-15}$   
(C)  $1 \times 10^{-12}$  (D)  $4 \times 10^{-12}$

**Sol.**

32. Consider the following cell reaction.

**[JEE-2011]**



At  $[\text{Fe}^{2+}] = 10^{-3} \text{ M}$ ,  $P(\text{O}_2) = 0.1 \text{ atm}$  and  $\text{pH} = 3$ , the cell potential at  $25^\circ \text{ C}$  is :

(A) 1.47 V (B) 1.77 V  
(C) 1.87 V (D) 1.57 V

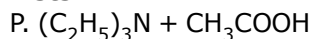
**Sol.**

34. The value of  $\Delta G$  ( $\text{kJ mol}^{-1}$ ) for the given cell is (take  $1 F = 96500 \text{ C mol}^{-1}$ )

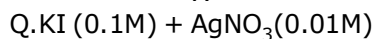
(A) -5.7 (B) 5.7  
(C) 11.4 (D) -11.4

**Sol.**

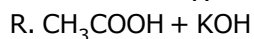
- 35.** An aqueous solution of X is added slowly to an aqueous solution of Y as in List I. The variation in conductivity of these reactions is given in List II. Match List I with List II and select the correct answer using the code given below the lists:

**Lists I**

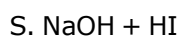
X Y



X Y



X Y



X Y

**List II**

1. Conductivity decreases and then increases
2. Conductivity decreases and then does not change much
3. Conductivity increases and then does not change much
4. Conductivity does not change much and then increases

**Sol.**

- 36.** The standard reduction potential data at  $25^\circ\text{C}$  is given below.

$$E^\circ (\text{Fe}^{3+}, \text{Fe}^{2+}) = +0.77 \text{ V};$$

$$E^\circ (\text{Fe}^{2+}, \text{Fe}) = 0.44 \text{ V}$$

$$E^\circ (\text{Cu}^{2+}, \text{Cu}) = +0.34 \text{ V}$$

$$E^\circ (\text{Cu}^+, \text{Cu}) = +0.52 \text{ V}$$

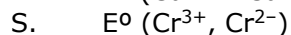
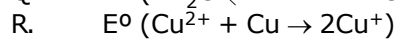
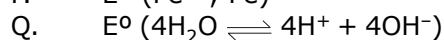
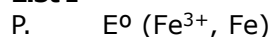
$$E^\circ [\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}] = +1.23 \text{ V};$$

$$E^\circ [\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-] = +0.40 \text{ V}$$

$$E^\circ (\text{Cr}^{3+}, \text{Cr}) = -0.74 \text{ V};$$

$$E^\circ (\text{Cr}^{2+}, \text{Cr}) = 0.91 \text{ V}$$

Match  $E^\circ$  of the redox pair in List I with the values given in List II and select the correct answer using the code given below the lists :

**List I****List II**

1.  $-0.18 \text{ V}$

2.  $-0.4 \text{ V}$

3.  $-0.04 \text{ V}$

4.  $-0.83 \text{ V}$

**Sol.**

# Answers

## Answer Ex-I

## OBJECTIVE PROBLEMS (JEE MAIN)

- |       |       |       |       |       |
|-------|-------|-------|-------|-------|
| 1. C  | 2. A  | 3. B  | 4. A  | 5. C  |
| 6. A  | 7. C  | 8. B  | 9. B  | 10. B |
| 11. B | 12. B | 13. A | 14. C | 15. C |
| 16. D | 17. C | 18. B | 19. B | 20. C |
| 21. B | 22. C | 23. B | 24. D | 25. B |
| 26. C | 27. B | 28. B | 29. B | 30. D |
| 31. D | 32. C | 33. A | 34. A | 35. B |
| 36. A | 37. A | 38. B | 39. A | 40. C |
| 41. C | 42. D | 43. C | 44. C | 45. C |
| 46. C | 47. C | 48. B | 49. A | 50. D |

## Answer Ex-II

## OBJECTIVE PROBLEMS (JEE ADVANCED)

- |       |                            |       |       |       |
|-------|----------------------------|-------|-------|-------|
| 1. CD | 2. BCD                     | 3. AB | 4. BC | 5. AD |
| 6. B  | 7. A                       | 8. A  | 9. D  | 10. B |
| 11. C | 12. A                      | 13. B | 14. A | 15. B |
| 16. B | 17. B                      | 18. C | 19. A | 20. B |
| 21. C | 22. A                      | 23. C | 24. A | 25. A |
| 26. B | 27. A-PQ, B-PQ, C-QR, D-PS |       |       |       |

**Answer Ex-III****SUBJECTIVE PROBLEMS (JEE ADVANCED)**

1. (a)  $2\text{Ag} + \text{Cu}^{2+} \rightarrow 2\text{Ag}^+ + \text{Cu}$ ,  
(c)  $2\text{Cl}^- + 2\text{Ag}^+ \rightarrow 2\text{Ag} + \text{Cl}_2$ ,
- (b)  $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$   
(d)  $\text{H}_2 + \text{Cd}^{2+} \rightarrow \text{Cd} + 2\text{H}^+$
2. (a)  $\text{Zn}|\text{Zn}^{2+}||\text{Cd}^{2+}|\text{Cd}$ ,  
(c)  $\text{Pt}|\text{Fe}^{2+}, \text{Fe}^{3+}||\text{Cr}_2\text{O}_7^{2-}, \text{H}^+, \text{Cr}^{3+}|\text{Pt}$
- (b)  $\text{Pt}|\text{H}_2|\text{H}^+||\text{Ag}^+|\text{Ag}$
3. 1.61 V                      4. 1.35 V                      5. - 0.80 V, NO
6. 0.53 V, disproportionation                      7. -0.0367 V                      8.  $E = 1.159 \text{ V}$
9.  $K_c = 1.864 \times 10^{107}$ ,  $\Delta G^\circ = -611.8 \text{ kJ}$                       10.  $n = 2$                       11.  $E = 0.059$
12.  $E^\circ_{\text{Cell}} = +0.01 \text{ V}$ ,  $E_{\text{Cell}} = -0.0785 \text{ V}$ , correct representation is  $\text{Pb}|\text{Pb}^{2+}(10^{-3}\text{M})||\text{Sn}^{2+}(1\text{M})|\text{Sn}$
13.  $[\text{Cu}^{2+}] = 2.97 \times 10^{-12} \text{ M}$  for  $E = 0$                       14.  $E = -0.81 \text{ V}$                       15. 0.52 V, 0.61 V
16. 0.0295 V                      17. 0.0295 V                      18.  $\text{pH} = 4$                       19.  $K_c = 7.6 \times 10^{12}$
20.  $K_c = 1.96 \times 10^{26}$                       21.  $K_w \approx 10^{-14}$                       22.  $E^\circ = 0.7826 \text{ V}$                       23.  $-1.30 \times 10^3 \text{ kJ/mol}$
24. (a)  $6.02 \times 10^{22}$  electrons lost, (b)  $1.89 \times 10^{22}$  electrons gained, (c)  $1.80 \times 10^{23}$  electrons gained
25. (a) 0.75 F, (b) 0.69 F, (c) 1.1 F                      26. (i) 54 gm, (ii) 16.35 gm
27.  $1.023 \times 10^5 \text{ sec}$                       28. 0.112 L                      29. Rs. 0.75 x
30. (i) 2.1554 gm ; (ii) 1336.15 sec                      31. 115800C, 347.4 kJ                      32.  $t = 193 \text{ sec}$
33.  $A = 114$ ,  $Q = 5926.8\text{C}$                       34. Final weight = 9.6g, 0.01 Eq of acid
35.  $t = 93.65 \text{ sec}$                       36. 60%                      37. 1.825 g
38. 2 M                      39.  $419 \text{ S cm}^2 \text{ equivalent}^{-1}$
40.  $0.00046 \text{ S cm}^{-1}$ ; 2174 ohm cm                      41. (i)  $6.25 \times 10^5 \text{ ohm}$ , (ii)  $1.6 \times 10^{-6} \text{ amp}$
42.  $0.0141 \text{ mho g equiv}^{-1} \text{ m}^2$ ,  $0.141 \text{ mho m}^{-1}$                       43. (i)  $232 \text{ Mho cm}^2 \text{ mol}^{-1}$ , (ii)  $116 \text{ Mho cm}^2 \text{ equivalent}^{-1}$
44.  $523.2 \times 10^{-4} \text{ mho cm}^2 \text{ mol}^{-1}$                       45. 0.865                      46. (i)  $390.6 \text{ S cm}^2 \text{ mol}^{-1}$  (ii) 12.32 %
47.  $1.33 \times 10^{-4} \text{ gm/litre}$                       48.  $8.74 \times 10^{-11} \text{ mole}^2/\text{litre}^2$
49.  $\alpha = 0.435$ ,  $k = 6.7 \times 10^{-4}$                       50. (i) 6.98 (ii)  $1.08 \times 10^{-14}$
51.  $[\text{Cu}^{2+}] = 10^{-4}\text{M}$                       52.  $\text{pH} = 6.61$                       53.  $K_a = 6.74 \times 10^{-4}$                       54. 1.39 V
55. -0.46 V                      56. (ii). 1.27 V, (iii) 245.1 kJ                      57.  $E^\circ = -0.22 \text{ V}$
58.  $h = 2.12 \times 10^{-2}$ ,  $K_h = 1.43 \times 10^{-5} \text{ M}$                       59. 0.95 V                      60.  $K_{sp} = 1.1 \times 10^{-16}$



61.  $[\text{Br}^-] : [\text{Cl}^-] = 1 : 200$  62.  $E^\circ = -0.1511 \text{ V}$  63.  $-0.037 \text{ V}$   
 64.  $1.536 \times 10^{-5} \text{ M}^3$  65.  $1.66 \text{ V}$  66.  $-1.188 \text{ V}$  67.  $E^\circ = 0.71 \text{ V}$   
 68.  $K_f = 8.227 \times 10^{63}$  69.  $0.372 \text{ V}, -0.307 \text{ V}$  70.  $K = 10^{268}$   
 71.  $\text{Ti}^+ = 10^{-8}$ ;  $\text{Co}^{3+} = 2 \times 10^{-8}$  72.  $43.456 \text{ g}$   
 73.  $42.2\%$  74.  $V(\text{O}_2) = 99.68 \text{ mL}, V(\text{H}_2) = 58.46 \text{ mL}, \text{Total vol.} = 158.1 \text{ mL}$   
 75.  $57.5894 \text{ gm}$  76.  $1.9 \text{ million year}$  77.  $1.21 \times 10^5 \text{ coulomb}$   
 78. (a)  $-0.124 \text{ V}$ , (b)  $7.1$ , (c) calomel electrode 79.  $-0.167 \text{ V}$   
 80.  $0.1456 \text{ ampere}$  81.  $3.29 \text{ cm}$  82.  $4.25 \times 10^{-8} \text{ metre}$  83.  $0.1934 \text{ gm/litre}$   
 84.  $K_{sp} = 7.682 \times 10^{-17}$  85.  $E = 0.395 \text{ V}$

**Answer Ex-IV****PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

1. B 2. C,D 3. C 4. C 5. B 6. C 7. A  
 8. D 9. C 10. C 11. A 12. C 13. B 14. D  
 15. B 16. C 17. C 18. A 19. D 20. C 21. B

**LEVEL – II****JEE ADVANCED**

1.  $K_c = 6.26 \times 10^7$  2.  $K_{sp} = 2.287 \times 10^{-12}$  3. A  
 4. B 5.  $7.95 \times 10^{-5} \text{ M}$  6. decrease with time 7. C  
 8. B 9. C 10.  $\Delta H^\circ = -49987 \text{ Jmol}^{-1}, \Delta S^\circ = -96.5 \text{ Jmol}^{-1} \text{ K}^{-1}, s = 1.47 \times 10^{-5}$   
 11. A 12. C 13.  $0.05 \text{ M}$  14. B 15.  $K_c = 10^{10}$   
 16. B 17. (a)  $E^\circ = 0.59 \text{ V}, \log_{10} K_{sp} = -10$ , (b)  $52.8, 10^{-6} \text{ moles}$  18. A  
 19. A 20. D 21.  $55 \text{ S m}^{-1}$  22. B 23. D  
 24. D 25. C 26. D 27. B 28. ABD  
 29. AB 30. B 31. C 32. D 33. B 34. D  
 35. A 36. D

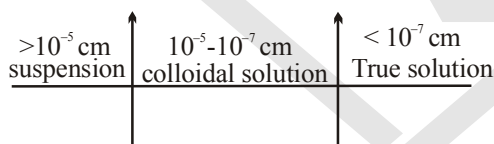
# **SURFACE CHEMISTRY**

Surface chemistry deals with phenomena that occur at the surfaces or interfaces. Many important phenomena, noticeable amongst these being corrosion, electrode processes, heterogeneous catalysis, dissolution and crystallisation occur at interfaces. The subject of surface chemistry finds many applications in industry, analytical work and daily life situations.

## **DISTINCTION BETWEEN TRUE SOLUTION, COLLOIDAL SOLUTION AND SUSPENSION :**

<b>Name of property</b>	<b>True solution</b>	<b>Colloidal solution</b>	<b>suspension</b>
1. Particle size	$<10^{-7}$ cm	$10^{-7}$ to $10^{-5}$ cm	$> 10^{-5}$ cm
2. Visibility	Not visible with any of the optical means	Images are visible under Ultra microscope	visible with naked eye
3. Separation with filter	Not possible	Not possible	Possible
4. Diffusion	Diffuses readily	Diffuse very slowly	Does not diffuse
5. Nature	Homogeneous	Heterogeneous	Heterogeneous
6. Setting	Does not settle	Settle under centrifuge	Settles under influence of gravity
7. Tyndall effect	Does not show	Shows	May or may not show
8. Brownian movement	Does not show	Shows	may show

## **PARTICLE SIZE :**



## **PHASE OF COLLOIDS :**

A colloidal system is heterogeneous in character. It consists of two phases, namely a dispersed phase and a dispersion medium.

(a) **Dispersed Phase (DP)** : It is the component present in small proportion and is just like a solute in a true solution. For example, in the colloidal state of sulphur in water, the former acts as a dispersed phase.

(b) **Dispersion Medium (DM)** : It is normally the component present in excess and is just like a solvent in a solution.

The particles of the dispersed phase are scattered in the dispersion medium in a colloidal system.

## **CLASSIFICATION OF COLLOIDS :**

Colloids can be classified in a number of ways based upon some of their important characteristics.

(1) **Physical state of Dispersed Phase & Dispersion Medium:**

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gaseous, eight types of colloidal system are possible. A gas mixed with another gas forms a homogeneous mixture and not a colloidal system. Typical examples of various type alongwith their characteristic names are given in table.

**Common Colloidal System**

<b>DP</b>	<b>DM</b>	<b>Colloidal system</b>	<b>Examples</b>
Gas	Liquid	Foam or froth	Soap sols, lemonade froth, whipped cream.
Gas	Solid	Solid foam	Pumice stone, styrene, foam, foam rubber.
Liquid	Gas	Aerosols of Liquids	Fog, clouds, fine insecticide spray, mist.
Liquid	Liquid	Emulsions	Milk, hair cream
Liquid	Solid	Gels	Cheese, butter, boot polish, table jellies, curd.
Solid	Gas	Aerosols of Solid	Smoke, dust
Solid	Liquid	Sols	Most paint, starch dispersed in water, gold sol, muddy water, cell fluids, inks.
Solid	Solid	Solid sols	Ruby glass, some gem stones.

(2) **Based on dispersion medium**

1. Water	:	Hydrosols
2. Alcohol	:	Alcosols
3. Gases	:	Aerosols
4. benzene	:	benzosol
5. solid	:	gel

Some colloids, such as gelatin, can behave both as a sol and a gel. At high temperature and low concentration of gelatin, the colloid is a hydrosol. But at low temperature and high gelatin concentration, the hydrosol can change into a gel.

- (3) **Based on interaction or affinity of phases :** On the basis of the affinity or interaction between the dispersed phase and the dispersion medium, the colloids may be classified into two types :

(i) **Lyophilic Colloids :** The colloidal system in which the particle of dispersed phase have great affinity for the dispersion medium, are called lyophilic (solvent-loving) colloids. In such colloids, the dispersed phase does not get easily precipitated and the sols are more stable. Such colloidal systems, even if precipitated, may be reconverted to the colloidal state by simply agitating them with the dispersion medium. Hence lyophilic colloids are reversible. When the dispersion medium is water, these are called hydrophilic colloids. Some common examples of lyophilic colloids are gum, gelatin, starch, rubber, proteins, etc.

(ii) **Lyophobic colloids :** The colloidal system in which the dispersed phase have no affinity for the dispersion medium are called lyophobic (solvent hating) colloids. They are easily precipitated (or coagulated) on the addition of small amounts of the electrolyte, by heating or by shaking. They are less stable and irreversible. When the dispersion medium is water, these are known as hydrophobic colloids. Examples of lyophobic colloids include sols of metals and their insoluble compounds like sulphides and oxides.

The essential differences between the lyophilic and lyophobic colloids are summarised in table.

#### ***Difference between Lyophilic and Lyophobic sols***

<b>Property</b>	<b>Lyophilic sols/hydrophilic</b>	<b>Lyophobic/hdrophobic sols</b>
1. Nature	Reversible	Irreversible
2. Preparation	They are prepared very easily by shaking or warming the substance with dispersion medium. They do not required any electrolyte for stabilization.	They are difficult to prepare, Special methods are used. Addition of stabiliser is essential for their stability.
3. Stability	They are very stable and are not easily coagulated by electrolytes.	They are generally unstable and get easily coagulated on addition of electrolytes.
4. Charge	Particles carry no or very little charge depending upon the pH of the medium.	Colloidal particles have characteristic charge (positive or negative)
5. Viscosity	Viscosity is much higher than that of the medium.	Viscosity is nearly the same as that of the medium

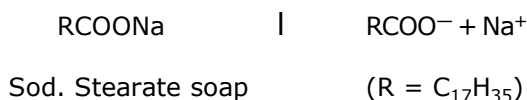
6.	Surface Tension	Surface tension is usually less than that of the medium.	Surface tension is nearly the same as that of the medium.
7.	Migration in electric field	The particles may or may not migrate in an electric field.	The colloidal particles migrate either towards cathode or anode in an electric field.
8.	Solvation	Particles are heavily solvated.	Particles are not solvated.
9.	Visibility	The particles cannot be seen under ultra microscope.	The particles though invisible, can be seen under ultra microscope.
10.	Tyndall effect	Less distinct.	More distinct.
11.	Action of electrolyte	Large amount of electrolyte is required to cause coagulation.	Small amount of electrolyte is sufficient to cause coagulation.
12.	Examples	Mostly organic substances e.g. starch, gums, proteins, gelatin, rubber etc.	Generally inorganic substance e.g., metal sols, sulphides and oxides sols.
(4)	<b>Based on type of particles of the dispersed phase :</b> Depending upon the molecular size, the colloidal system has been classified into three classes :		

(i) **Multimolecular colloids :** The multimolecular colloidal particles consists of aggregate of atoms of small molecules with diameters less than  $10^{-9}$  m or 1 nm.

For example, a sol. of gold contains particles of various sizes having several atoms. A sol. of sulphur consists of particles containing a thousand or so  $S_2$  molecules. These particles are held together by vander Waal's forces. These are usually lyophobic sols for example gold sol.

(ii) **Macromolecular colloids :** The macromolecular colloidal particles themselves are large molecules. They have very high molecular weights varrying from thousands to millions. These substances are generally polymers. Naturally occurring macromolecules are such as starch, cellulose and proteins. Artificial macromolecules are such as polyethylene, nylon, polysyrene, dacron, synthetic rubber, plastics, etc. The size of these molecules are comparable to those of colloidal particles and therefore, their dispersion known as macromolecular colloids. Their dispersion also resemble true solutions in some respects. For example - Starch, cellulose, proteins and enzymes.

(iii) **The associated colloids or micelles :** These colloids behave as normal electrolytes at low concentrations but colloids at higher concentrations. This is because at higher concentrations, they form aggregated (associated) particles called micelles. Soap and synthetic detergents are examples of associated colloids. They furnish ions which may have colloidal dimensions.



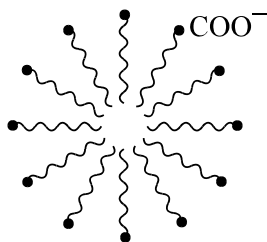
The long-chain  $\text{RCOO}^-$  ions associate or aggregate at higher concentrations and form micelles and behave as colloids. They may contain 100 or more molecules.

Sodium stearate  $\text{C}_{17}\text{H}_{35}\text{COONa}$  is an example of an associated colloid. In water it gives  $\text{Na}^+$  and stearate,  $\text{C}_{17}\text{H}_{35}\text{COO}^-$  ions. These ions associate to form micelles of colloidal size.

*Colloids which behave as normal electrolytes at low concentration, but exhibit colloidal properties at higher concentration due to the formation of aggregated particles called micelles are referred to as associated colloids. The micelles are formed by the association of dispersed particles above a certain concentration and certain minimum concentration is required for the process of aggregation to take place. The minimum concentration required for micelle formation is called micellisation concentration (CMC) and its value depends upon the nature of the dispersed phase. For soaps CMC is  $10^{-3}$  -  $10^{-4}$  M.*

#### **Mechanism of Micelle Formation :**

Micelles are formed by surface active molecules called surfactants such as soaps and detergents. These molecules have lyophilic group at one end and a lyophobic group at the other end. Let us take the example of a soap (say sodium oleate,  $\text{C}_{17}\text{H}_{33}\text{COO}^- \text{Na}^+$ ). The long hydrocarbon part of oleate radical ( $\text{C}_{17}\text{H}_{33}-$ ) is lyophobic end while  $\text{COO}^-$  part is lyophilic end. When the concentration of the solution is below its CMC, sodium oleate behaves as a normal electrolyte and ionises to give  $\text{C}_{17}\text{H}_{33}\text{COO}^-$  and  $\text{Na}^+$  ions. When the concentration exceeds CMC, the lyophobic part starts receding away from the solvent and tends to approach each other. However, the polar  $\text{COO}^-$  ends tend to interact with the solvent (water). This finally leads to the formation of bigger molecules having the dimensions of colloidal particles. Thus 100 or more oleate ions are grouped together in a spherical way keeping their hydrocarbon parts inside and the  $-\text{COO}^-$  part remains projected in water.



**LIST OF SURFACTANTS AND THEIR CRITICAL MICELLE CONCENTRATION (CMC)**

Surfactant	CMC (g/1)	Temp.(°C)
<i>Anionic</i>		
$\text{CH}_3(\text{CH}_2)_6\text{COONa}$	$6.5 \times 10^{-1}$	20
$\text{CH}_3(\text{CH}_2)_{10}\text{COONa}$	5.6	20–70
$\text{CH}_3(\text{CH}_2)_7\text{OSO}_3\text{Na}$	$3.0 \times 10^{-1}$	25–50
$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$	2.6	25–60
$\text{CH}_3(\text{CH}_2)_5\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	9.8	75
$\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	$4.0 \times 10^{-1}$	50–75
<i>Cationic</i>		
$\text{CH}_3(\text{CH}_2)_9\text{NH}_2\cdot\text{HCl}$	8.5	25
$\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\text{HCl}$	2.7	30–50
$\text{CH}_3(\text{CH}_2)_7\text{N}(\text{CH}_3)_3\text{Br}$	$7.8 \times 10^{-1}$	25
$\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3\text{Br}$	5.4	25
<i>Non-ionic</i>		
$\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_{11}\text{O}_6$	7.3	25
$\text{C}_{12}\text{H}_{20}\text{O}_9(\text{C}_{16}\text{H}_{31}\text{O}_2)_2$	$1.1 \times 10^{-2}$	20
$\text{CH}_3(\text{CH}_2)_{10}\text{COOC}_{12}\text{H}_{21}\text{O}_{10}$	$7.1 \times 10^{-3}$	50

**PREPARATION OF COLLOIDAL SOLUTIONS**

- (1) **Preparation of lyophilic sols :** The colloidal solutions of lyophilic colloids like starch, glue, gelatin etc., can be readily prepared by dissolving these substances in water either in cold or on warming. Solutions of colloidal electrolytes such as soaps and dye stuffs can also be prepared similarly.
- (2) **Preparation of lyophobic sols :** To get a substance in colloidal form either the substance in bulk is broken down into fine particles of colloidal dimension ( $1\text{\AA}$  to  $10^3\text{\AA}$ ) or increasing the size of molecular particles as to form larger aggregates. In some cases, a third substance is usually added to increase the stability of the sol. These substances are called stabilizers. Thus, there are two ways by which the lyophobic sols can be prepared :

(i) **Dispersion methods :** By splitting coarse aggregates of a substance into colloidal size.

(ii) **Condensation methods :** By aggregating very small particles (atoms, ions or molecules) into colloidal size.

**S. No. Dispersion methods**

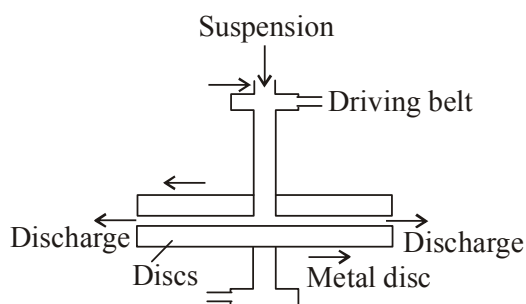
- Mechanical dispersion
- Electro-dispersion
- Ultrasonic dispersion
- Peptisation

**Condensation methods**

- Exchange of solvents
- Change of physical state
- Chemical methods :
  - Double decomposition
  - Oxidation
  - Reduction
  - Hydrolysis

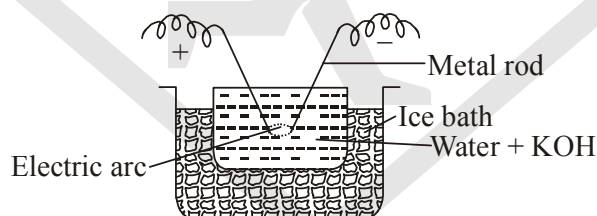
**Dispersion Methods**

- (1) **Mechanical dispersion :** Solid material is first finely ground by usual methods. It is then mixed with dispersion medium which gives a coarse suspension. The suspension is now introduced into the colloid mill. The simplest form of colloid mill consists of two metal discs held at a small distance apart from one another and capable of revolving at a very high speed (about 7000 revolutions per minute) in opposite directions. The particles are ground down to colloidal size and are then dispersed in the liquid. A stabilizer is often added to stabilize the colloidal solution. Colloidal graphite (a lubricant) and printing ink



are made by this method. Tannin is used as a stabilizer in the preparation of colloidal graphite and gum arabic in lampblack colloidal solution (Indian ink).

- (2) **Electro-dispersion (Bredig's arc method) :** This method is suitable for the preparation of colloidal solutions of metals like gold, silver, platinum, etc. An arc is struck between the metal electrodes under the surface of water containing some stabilizing agents such as a track of KOH. The water is cooled by immersing the



container in an ice bath. The intense heat of the arc vaporises some of the metal which condenses under cold water.

**Note :** (1) This method is not suitable when the dispersion medium is an organic liquid as considerable charring occurs.

(2) This method comprises both dispersion and condensation.

- (3) **Ultrasonic dispersion :** The sound waves of high frequency are usually called ultrasonic waves. These waves can be produced when quartz crystal discs are connected with a high frequency generator. The application of ultrasonic waves for the preparation of colloidal solutions was first introduced by Wood and Loomis, in 1927. Various substances like oils, mercury, sulphur, sulphides and oxides of metals can be dispersed into colloidal state very easily with the help of ultrasonic waves.



- (4) **Peptization :** The dispersion of a freshly precipitated material into colloidal solution by the action of an electrolyte in solution is termed peptization. The electrolyte used is called a peptizing agent.

A few examples of sols obtained by peptization are :

(i) Freshly prepared ferric hydroxide on treatment with a small amount of ferric chloride solution at once forms a dark reddish brown solution. Ferric chloride acts as a peptizing agent.

(ii) Freshly prepared stannic oxide on treatment with a small amount of dilute hydrochloric acid forms a stable colloidal solution of stannic oxide.

(iii) Freshly precipitated silver chloride can be converted into a colloidal solution by a small amount of hydrochloric acid.

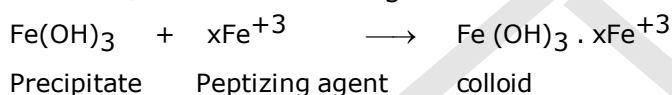
(iv) Cadmium sulphide can be peptized with the help of hydrogen sulphide.

The process of peptization thus involves the adsorption of suitable ions (supplied by the electrolyte added—particularly a common ion) and electrically charged particles then split from the precipitate as colloidal particles.

**Important peptizing agents :** Sugar, Gum, Gelatin & Electrolytes.

#### Example

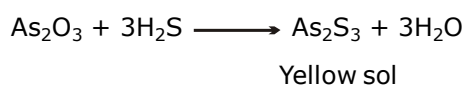
Freshly prepared ferric hydroxide can be converted into colloidal state by shaking it with water containing  $\text{Fe}^{+3}$  or  $\text{OH}^-$  or  $\text{FeCl}_3$



#### Condensation Methods

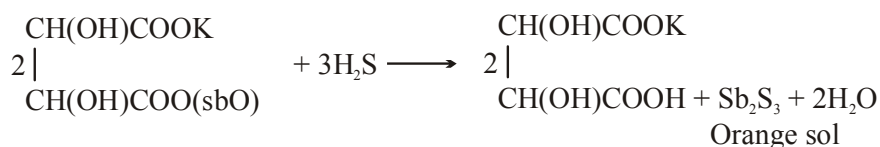
- (1) **By exchange of solvents :** If a solution of sulphur or phosphorus prepared in alcohol is poured into water, a colloidal solution of sulphur or phosphorus is obtained due to low solubility of sulphur or phosphorus in water. Thus, there are a number of substances whose colloidal solutions can be prepared by taking a solution of the substance in one solvent and pouring it into another solvent in which the substance is relatively less soluble.
- (2) **By change of physical state :** Colloidal solutions of certain elements such as mercury and sulphur are obtained by passing their vapour through cold water containing a stabilizer (an ammonium salt or a citrate)
- (3) **Chemical methods :** The chemical methods involve chemical reactions in a medium in which the dispersed phase is sparingly soluble. A condition of supersaturation is produced but the actual precipitation is avoided. Some familiar reactions used are :

(a) **Double decomposition :** (i) Arsenious sulphide sol : A 1% solution of arsenious oxide is prepared in hot water. The solution is cooled, filtered and is then gradually in hot water saturated with hydrogen sulphide. This is continued till an intense yellow-coloured solution is obtained. Excess of  $\text{H}_2\text{S}$  is removed by bubbling hydrogen through the solution.

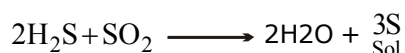


(ii) Antimony sulphide sol : A 0.5% solution of potassium antimonyl tartarate is added drop by drop

to water saturated with  $\text{H}_2\text{S}$ , whilst  $\text{H}_2\text{S}$  is being passed through the solution. Orange coloured solution of antimony sulphide is obtained.

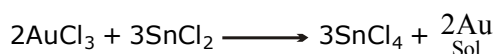


**(b) Oxidation :** A colloidal solution of sulphur is obtained by passing  $\text{H}_2\text{O}$  into a solution of sulphur dioxide.

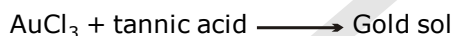
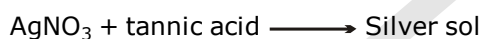


Sulphur sol can also be obtained when  $\text{H}_2\text{S}$  is bubbled through an oxidising agent (bromine water or nitric acid).

**(c) Reduction :** Colloidal solutions of metals like gold, silver, platinum, lead, etc., can be obtained when their salts solutions are acted upon by reducing agents.



Organic reducing agents such as formaldehyde, phenyl hydrazine, tannic acid, etc., can also be used.



**(d) Hydrolysis :** Colloidal solutions of some salts can be prepared by hydrolysis. A colloidal solution of ferric hydroxide is obtained by boiling a dilute solution of ferric chloride.]

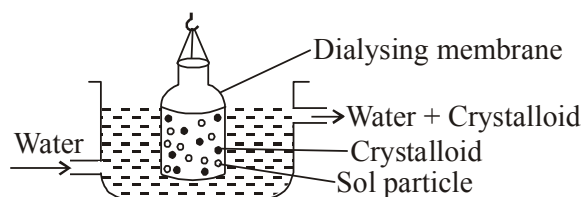


The colloidal solution of silicic acid is also obtained by hydrolysis of dilute solution of sodium silicate with 4N hydrochloric acid which is added drop by drop with constant stirring.

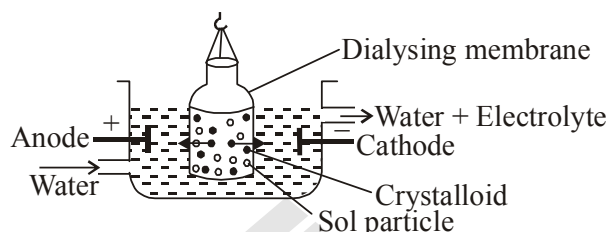
### **PURIFICATION OF COLLOIDAL SOLUTIONS**

Colloidal solutions prepared by above methods generally contain excessive amount of electrolytes and some other soluble impurities. The presence of traces of electrolyte is essential for the stability of the colloidal solution but larger quantities coagulate it. It is, therefore, necessary to reduce the concentration of these soluble impurities to a requisite minimum. The process used for reducing of these impurities to a requisite minimum is known as purification of colloidal solution. The purification of colloidal solution is carried out by the following methods.

**(i) Dialysis\* :** It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through suitable membrane. Since, particles in true solution (ions or smaller molecules) can pass through animal membranes (bladder) or parchment paper or cellophane sheet but colloidal particles do not, the above can be used for dialysis. The apparatus used for this purpose is called dialyser. A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flown figure. The molecules and ions diffuse through the membrane into the outer water and pure colloidal solution is left behind.



**(ii) Electro-dialysis :** Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only electrolyte. The process is then named electro-dialysis. The colloidal solution is placed between two electrodes while pure water is taken in a compartment on each side. Electrodes are fitted in the compartment as shown in figure the ions present in the colloidal solution migrate out to the oppositely charged electrodes.



**(iii) Ultrafiltration :** Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by especially prepared filters, which are permeable to all substances except the colloidal particles.

Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with collodion solution and subsequently hardened by soaking in formaldehyde. The usual collodion is a 4% solution of nitro-cellulose in a mixture of alcohol and ether. An ultrafilter paper may be prepared by soaking the filter paper in a collodion solution and hardened by formaldehyde and finally drying it. Thus, by using ultrafilter paper, the colloidal particles are separated from rest of the materials. Ultrafiltration is a slow process. To speed up the process, pressure or suction is used.

The colloidal particles left on the ultrafilter paper are then stirred with fresh dispersion medium (solvent) to get a pure colloidal solution.

### PROPERTIES OF COLLOIDAL SOLUTIONS :

#### (1) **Physical properties :**

(i) **Heterogeneity :** Colloidal solutions are heterogeneous in nature consisting of two phases viz, the dispersed phase and the dispersion medium. Experiments like dialysis and ultra filtration clearly indicate the heterogeneous character of colloidal system. Recent investigations however, shown that colloidal solutions are neither obviously homogeneous nor obviously heterogeneous.

(ii) **Filterability :** Colloidal particles readily pass through ordinary filter papers. It is because the size of the pores of the filter paper is larger than that of the colloidal particles.

(iii) **Non-settling nature :** Colloidal solutions are quite stable as the colloidal particles remain suspended in the dispersion medium indefinitely. Thus there is no effect of gravity on the colloidal particles.

(iv) **Colour :** The colour of the colloidal solution is not always the same as the colour of the substances in the bulk. The colour of the colloidal solution depends upon the following factors :

- Size and shape of colloidal particles.
- Wavelength of the source of light.
- Method of preparation of the colloidal solution.
- Nature of the colloidal solution.
- The way an observer receives the light, i.e., whether by reflection or by transmission.

- (f) **Stability :** Colloidal solutions are quite stable. Only a few solutions of larger particles may settle but very slowly.

### Examples :

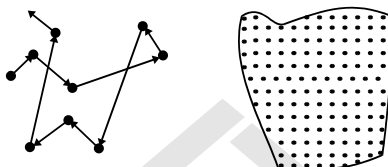
- (i) Finest gold is red in colour. As the size of particles increases, it becomes purple.
- (ii) Dilute milk gives a bluish tinge in reflected light whereas reddish tinge in transmitted light.

### (2) Mechanical Properties :

- (a) **Brownian movement :** Colloids particles exhibit a ceaseless random and swarming motion. This kinetic activity of particles suspended in the liquid is called Brownina movement. Robert Brown first observed this motion with pollen grains suspended in water.

**Cause of movement :** Brownian movement is due to bombardment of the dispersed particles by molecules of the medium. The Brownian movement (figure) depends upon the size of sol. particles. With the increase in the size of the particle, the chance of unequal bombardment decrease, and the Brownian movement too disappears. It is due to the fact that the suspension fails to exhibit this phe-nomenon.

It should be noted that Brownian movement does not change with time but changes with temperatures.



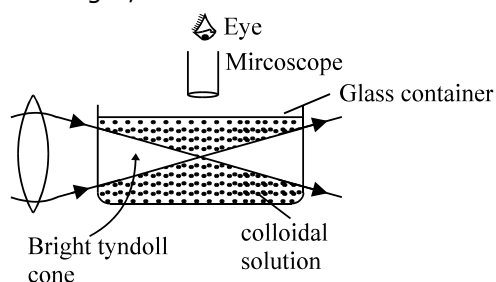
### Importance :

- (i) Brownian movement is a direct demonstration of the assumption that the molecules in a gas or solution are in a state of constant ceaseless motion. Thus it confirms kinetic theory.
  - (ii) Brownian movement does not allow the colloidal particles to settle down due to gravity and thus is responsible for their stability.
  - (iii) Brownian movement helps to calculate the Avogadro's number (Detail beyond the scope of the book).
- (b) **Sedimentation :** Heavier sol. particle tend to settle down very slowly under the influence of gravity. This phenomenon is called sedimentation.

### (3) Optical Properties (Tyndal Effect) :

When a strong and converging beam of light is passed through a colloidal solution, its path becomes visible (bluish light) when viewed at right angles to the beam of light (figure). This effect is called Tyndall effect. The light is observed as a bluish cone which is called Tyndall cone.

The Tyndall effect is due to scattering of light by the colloidal particles. The scattering of light cannot be due to simple reflection, because the size of the particles is smaller than the wave, length of the visible light and they are unable to reflect light waves. In fact, colloidal particles first absorb light and then a part of the absorbed light is scattered from the surface of the colloidal particles as a light of shorter wavelength. Since maximum scattering of light takes place at right angles to the place of incident light, it becomes visible when seen from that direction.



The Tyndall effect is observed under the following conditions :

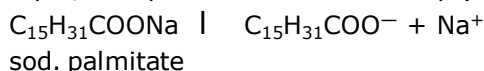
- (i) The diameter of the dispersed particles must not be much smaller than the wavelength of light employed.
- (ii) The refractive indices of the dispersed phase and the dispersion medium must differ widely. This condition is fulfilled by lyophobic colloids.

It is important to note that Tyndall effect is not shown by true solutions as their particles are too small to cause scattering. Tyndall effect has been used in devising ultramicroscope and in determining the number of colloidal particles in a colloidal solution.

(4) **Electrical Properties :**

**Origin of charge :** Various reasons have been given regarding the origin of charge on the colloidal particles. These are given below :

- (i) **Frictional electrification :** It is believed to be frictional due to the rubbing of the dispersed phase particles with medium molecules.
- (ii) **Dissociation of the surface molecules :** It leads to electric charge on colloidal particles. For example, an aqueous solution of a soap (sodium palmitate) dissociates into ions.



The  $\text{Na}^+$  ions pass into the solution while  $\text{C}_{15}\text{H}_{31}\text{COO}^-$  ions have a tendency to form aggregates due to weak attractive forces present in the hydrocarbon chains. Thus, the anions which are of colloidal size bear negative charge.

- (iii) **Preferential adsorption of ions from solution :** The charge on the colloidal particles is generally acquired by preferentially adsorbing positive or negative ions from the electrolyte. Thus  $\text{AgCl}$  particles can adsorb  $\text{Cl}^-$  ions from chloride solutions and  $\text{Ag}^+$  ions from excess  $\text{Ag}^+$  ions solutions; the sol. will be negatively charged in the first case and positively charged in the second case.
- (iv) **Capture of electron :** It is from air during preparation of sol. by Bredig's arc method.
- (v) **Dissociation of molecular electrolytes on the surface of particles :**  $\text{H}_2\text{S}$  molecules get adsorbed on sulphides during precipitation. By dissociation of  $\text{H}_2\text{S}$ ,  $\text{H}^+$  ions are lost and colloidal particles become negatively charged.

**Electrical charged sols.**

**Positively charged sols**

1. Ferric hydroxide, aluminium hydroxide
2. Basic dyes such as methylene blue
3. Haemoglobin

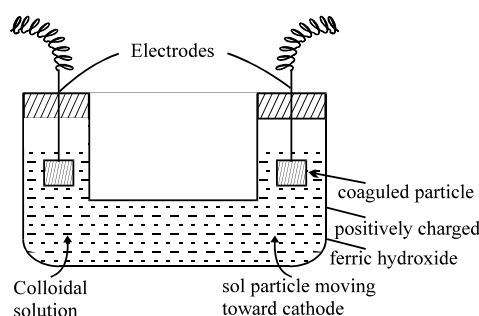
**Negatively charged sols**

- Metals such as Pt, Au, Ag, Metals sulphides, e.g. arsenious sulphide.
- Starch, clay, silicic acid.
- Acid dyes, such as eosin.

The two electrical properties of colloidal solutions are :

- (a) **Electrophoresis or Cataphoresis** and
- (b) **Electro-osmosis**

(a) **Electrophoresis or Cataphoresis :** In a colloidal solution, the colloidal particles are electrically charged and the dispersion medium has equal but opposite charge. Thus colloidal solution on the whole is electrically neutral. When an electric current is passed through a colloidal solution, the charged particles move towards the oppositely charged electrode where coagulate due to loss of charge.



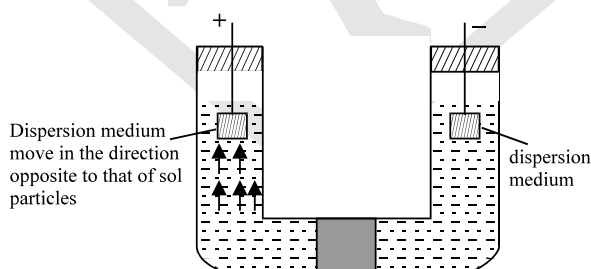
The phenomenon involving the migration of colloidal particles under the influence of electric field towards the oppositely charged electrode, is called electrophoresis or cataphoresis.

This phenomenon is used to determine the charge on the colloidal particles. For example, when a sol. of ferric hydroxide is taken in a U-tube and subjected to electric field, the ferric hydroxide (sol.) particles get accumulated near the cathode (figure). This shows that ferric hydroxide sol. particles are positively charged.

The sol. particles of metals and their sulphides are found to be negatively charged while those of metal hydroxides are positively charged. Basic dyes such as methylene blue haemoglobin are positively charged while acid dyes like are negatively charged.

(b) **Electro-osmosis :** The phenomenon involving the migration of the dispersion medium and not the colloidal particles under the influence of an electric field is electro-osmosis.

Take the pure solvent (dispersion medium) in two limbs of U-tube. In the lower middle portion of U-tube, a porous diaphragm containing the colloidal system is present which divides the U-tube in two sections. In each section of U-tube, an electrode is present, as shown in figure. When the electrode potential is applied to the electrodes, the solid phase of sol. (colloidal system) cannot move but the solvent (dispersion medium) moves through the porous diaphragm towards one of the electrodes. The direction of migration of dispersion medium due to electro-osmosis determines the charge on sol. particles e.g., if the dispersion medium moves towards the cathode (negative electrode), the sol. particles are also negatively charged because the dispersion medium is positively charged as on the whole colloidal solution is neutral.



(c) **Coagulation :** the colloidal sols are stable due to the presence of electric charges on the colloidal particles. Because of the electrical repulsion, the particles do not come close to one another to form precipitates. The removal of charge by any means will lead to the aggregation of particles and hence precipitation will occur immediately.

**This process by means of which the particles of the dispersed phase in a sol. are precipitated is known as coagulation.**

If the coagulated particles instead of settling at the bottom of the container, float on the surface of the dispersion medium, the coagulation is called *flocculation*.

Most of the sols are coagulated by adding an electrolyte of opposite sign. This is due to the fact that the colloidal particles take up the ions of electrolyte whose charges are opposite to that on

colloidal particles with the result that charge on the colloidal particles is neutralized. Thus coagulation takes place. For example, arsenic sulphide sol. (negatively charged) precipitated by adding barium chloride solution. It is due to the fact that the negatively charged particles of the sol. take up barium ions and get neutralized which lower the stability. As a result precipitation takes place.

It is observed that different amounts of different electrolytes is required to bring coagulation of a particular solution.

The minimum amount of an electrolyte required to cause precipitation of one litre of a colloidal solution is called coagulation value or flocculation value of the electrolyte for the sol.

The reciprocal of coagulation value is regarded as the *coagulating power*.

For example, the coagulation values of NaCl, BaCl<sub>2</sub> and AlCl<sub>3</sub> for arsenic sulphide sol. are 51, 0.69 and 0.093 millimoles/litre respectively. Thus their coagulating powers are  $\frac{1}{51}$ ,  $\frac{1}{0.69}$  and  $\frac{1}{0.093}$  i.e., 0.0196, 1.449 and 10.75 respectively.

The coagulation values of a few electrolytes for negatively charged arsenic sulphide and positively charged ferric hydroxide sol. are given in table given below. The valency of the coagulation ion (the ion whose charge is opposite to that of the colloidal particles) is also give.

#### Coagulation values of different electrolytes

##### Arsenic sulphide sol. (–Ve sol.)

##### Ferric hydroxide sol. (+Ve sol.)

Electrolyte	Valency of coagulating cation	coagulation value (millimoles/litre)	Electrolyte	Valency of coagulating anion	coagulation value (millimoles/litre)
K <sub>2</sub> SO <sub>4</sub>	1	63	KBr	1	138
NaCl	1	51	KNO <sub>3</sub>	1	132
KNO <sub>3</sub>	1	50	KCl	1	103
MgSO <sub>4</sub>	2	0.81	K <sub>2</sub> CrO <sub>4</sub>	2	0.320
BaCl <sub>2</sub>	2	0.69	K <sub>2</sub> SO <sub>4</sub>	2	0.215
AlCl <sub>3</sub>	3	0.093	K <sub>3</sub> Fe(Cn) <sub>6</sub>	3	0.096

From the above table, it is clear that the coagulating power of Al<sup>3+</sup> ions in precipitating the arsenic sulphide sol. is approximately 550 times more than that of sodium (Na<sup>+</sup>) or potassium (K<sup>+</sup>) ions. Again, it is observed that the negatively charged arsenic sulphide sol. is coagulated by cations while positively charged ferric hydroxide sol. is coagulated by anions.

**Hardy-Schulz rules :** H. Schulze (1882) and W.B. Hardy (1900) suggested the following rules to discuss the effect of electrolytes of the coagulation of the sol.

- (1) Only the ions carrying charge opposite to the one present on the sol. particles are effective to cause coagulation, e.g., the negative charged sol. is best coagulated by cations and a positive sol. is coagulated by anions.

- (2) The charge on coagulating ion influences the coagulation of sol.

In general, the coagulating power of the active ion increases with the valency of the active ion.

After observing the regularities concerning the sign and valency of the active ion, a law was proposed by Hardy and Schulz which is termed as Hardy-Schulze law which is stated as follows:

*"Higher is the valency of the active ion, greater will be its power to precipitate the sol."*

Thus, coagulating power of cations is in the order of  $\text{Al}^{3+} > \text{Ba}^{2+}$  or  $\text{Mg}^{2+} > \text{Na}^+$  or  $\text{K}^+$ .

Similarly, to coagulating the positively charged sol. the coagulating power of anion is in the order of  $[\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$

#### **Some other methods of coagulation :**

Apart from the addition of electrolyte, coagulation can also be carried out by following methods:

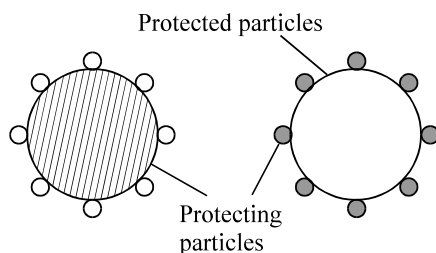
- (i) **By persistent dialysis :** It has been observed that traces of electrolytes are associated with the solution due to which it is stable. If the solution is subjected to prolonged dialysis, the traces of electrolytes are removed and coagulation takes place.
  - (ii) **By mutual coagulation of colloids :** When two sols of oppositely charges are mixed together in a suitable proportion, the coagulation takes place. The charge of one is neutralized by the other. For example, when negatively charged arsenic sulphide sol. is added to positively charged ferric hydroxide sol., the precipitation of both occurs simultaneously.
  - (iii) **By electrical method :** If the electrical charge of lyophobic sol. is removed by applying any electric field such as in electrophoresis, they also precipitate out.
  - (iv) By excessive cooling or by excessive heating.
- (5) **Colligative properties :** Colloidal solutions too exhibit colligative properties such as osmotic pressure, lowering of vapour pressure, depression in freezing point and elevation in boiling point. But the effect of colloidal particles on colligative properties except osmotic pressure is very small. This is due to the large size of colloidal particles. The number of colloidal particles produced by a given mass of colloid is much less than the number produced in a molecular solution, containing the same mass of solute. Hence the colligative effect in colloidal solutions is too less.

\*

#### **PROTECTIVE COLLOIDS :**

Lyophilic sols are more stable than the lyophobic sols. This is because, lyophilic colloids are extensively hydrated and these hydrated particles do not combine to form large aggregates.

Lyophobic sols are more easily coagulated by the addition of suitable electrolyte. To avoid the precipitation of lyophobic sol. by the addition of electrolyte, some lyophilic colloid is added to it. Such lyophilic colloid is called protective colloid and the action of lyophilic colloid by the electrolytes is known as protective anion. The substances commonly used as protective colloids are gelatin, albumin, gum arabic, casein, starch, glue etc. A gold sol. containing a little gelatin as protective colloid needs a very large amount of sodium chloride to coagulate the sol.





**Explanation :** The particles of the protective colloid get adsorbed on the particles of the lyophobic colloid, thereby forming a protective layer around it (figure). The protective layer prevents the precipitating ions from coming in contact with the colloidal particles.

According to a recent view, the increase in stability of the lyophobic colloid is due to the mutual adsorption of the lyophilic and lyophobic colloids. It is immaterial which is adsorbed on which. In fact the smaller particles, whether of the protective colloid or the lyophobic colloid, are adsorbed on the bigger particles.

**Gold number** of a protective colloid is a minimum weight of it in milligrams which must be added to 10 ml of a standard red gold sol so that no coagulation of the gold sol. (i.e. change of colour from red to blue) takes place when 1 ml of 10 % sodium chloride solution is rapidly added to it. Obviously, **smaller the gold number of a protective colloid, the greater is the protective action.**

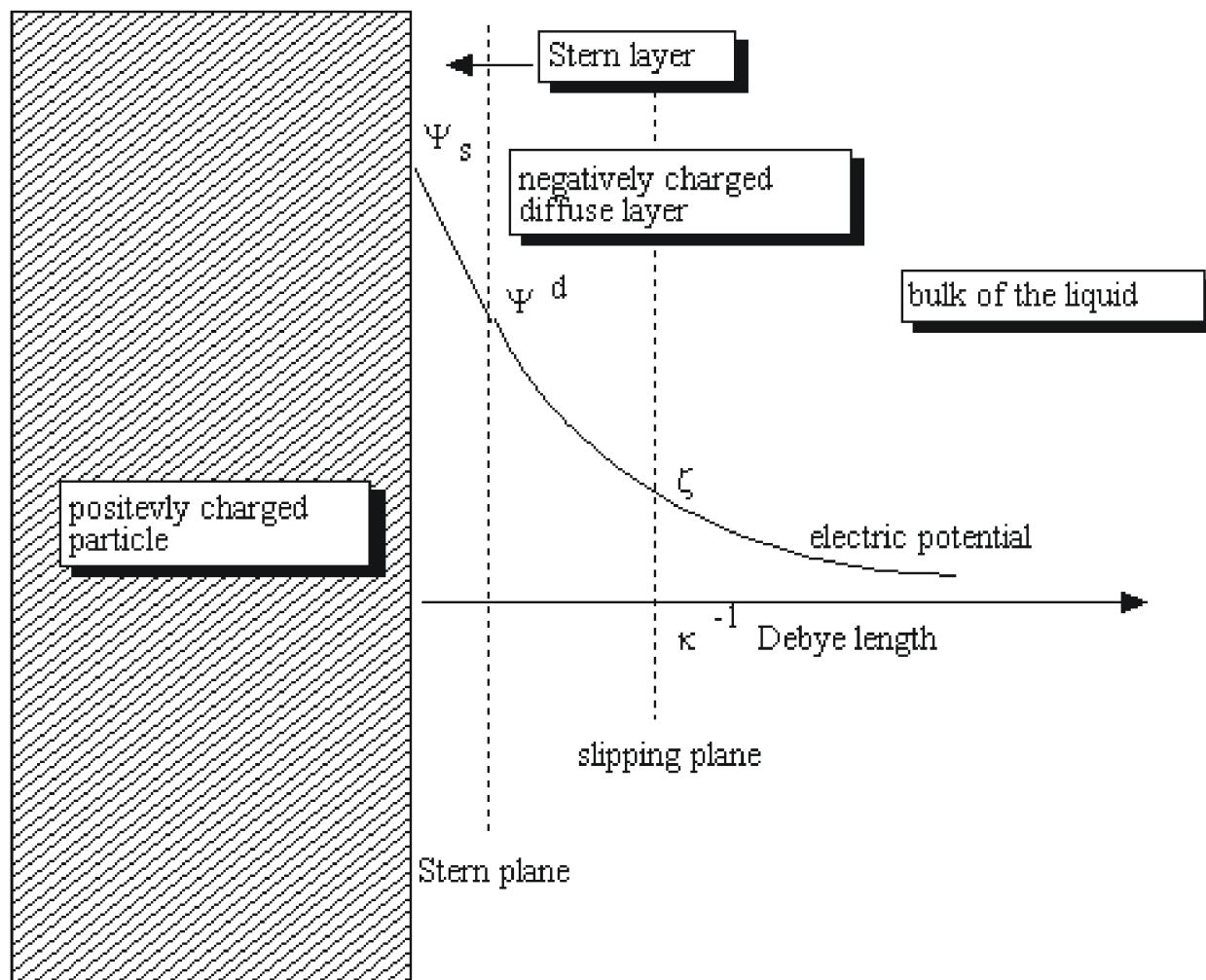
Protective colloid		Gold number
Gelatin	:	0.005
Haemoglobin	:	0.03
Albumin	:	0.15
Starch	:	2.5

**Isoelectric Point of Colloid :**

The hydrogen ion concentration at which the colloidal particles are neither positively charged nor negatively charged (i.e. uncharged) is known as isoelectric point of the colloid. At this point lyophilic colloid is expected to have minimum stability because at this point particles have no charge. The isoelectric point of gelatin is 4.7. This indicates that at pH = 4.7, gelatin has no electrophoretic motion. Below 4.7, it moves towards the cathode and above 4.7 it moves towards the anode. It is not always true, e.g., silicic acid has been found to have maximum stability at the isoelectric point.

**Electric double layer :**

*The surface of a colloidal particle acquires a positive or a negative charge by selective adsorption of ions carrying +ve or - ve charges respectively. The charged layer attracts counter ions from the medium which forms a second layer. Thus, an electrical double layer is formed on the surface of the particles i.e., one due to adsorbed ions and the other due to oppositely charged ions forming a diffused layer. This layer consists of ions of both the signs, but its net charge is equal and opposite to those adsorbed by the colloidal particles. The existence of charges of opposite signs on the fixed and diffused parts of the double layer creates a potential between these layers. This potential difference between the fixed charge layer and diffused layer of opposite charge is called electrokinetic potential or zeta potential.*



## **EMULSIONS**

An emulsion is a colloidal solution of a liquid. It may be defined as a heterogeneous system consisting of more than one immiscible liquids dispersed in one another in the form of droplets whose diameter, in general, exceeds  $0.1 \mu$ .

For example, milk is an emulsion in which small drops of liquid fat are dispersed in aqueous medium. Cod liver oil is an emulsion in which the water drops are dispersed in the oil. This means in most of the emulsions one of the liquid is water and the other liquid is oil. Here the term 'oil' is used to represent all organic substances which are soluble in water.

The emulsion are classified as :

- (1) **Oil in water type emulsion (O/W):** In this emulsion, oil is the dispersed phase and water is the dispersion medium. It is denoted by O/W or O in W. For example, milk (liquid fat dispersed in water), vanishing cream, etc.
- (2) **Water in oil type :** In this emulsion, water is the dispersed phase and oil is the dispersion medium. It is denoted by W/O or W in O. For example, butter, cod liver oil, cold cream, etc.

The type of emulsion obtained by agitating two immiscible liquids depends upon the relative amounts of two components liquids. The liquid that is in excess forms the dispersion medium. Thus,

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the two types of emulsions can be interconverted into each other by changing the concentration of one of the liquids.

**Distinction between two types of emulsions :** the two types of emulsions may be distinguished from each other in a number of ways.

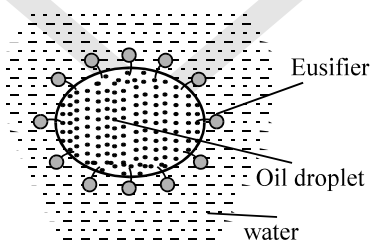
- (1) **Dye test :** It involves the addition of oil soluble dye to the emulsion under experiment. If the emulsion acquires the colour of the dye readily, it is water-in-oil type emulsion and if the emulsion remains colourless, it is oil-in-water type emulsion.
- (2) **Conductivity test :** It involves the addition of electrolyte to the emulsion under experiment. If the conductivity of the emulsion increases appreciably with the addition of electrolyte, it is oil-in-water type emulsion and if its conductivity is very small, it is water-in-oil type emulsion.
- (3) **Dilution test :** As a general rule, an emulsion can be diluted with the dispersion medium while the addition of the dispersed phase forms a separate layer. Thus, if an emulsion can be diluted with oil, it is water-in-oil type.

**Preparation of emulsion (Emulsification) :** Emulsification is the process which involves the preparation of emulsion. Generally, an emulsion is prepared by subjecting a mixture of the immiscible liquid to a distinct layer upon standing. The oil globules rise to form an upper layer while aqueous medium forms lower layers. To prevent the separation of layers and to get the stable emulsion, a small quantity of the third substance is added. This substance which stabilizes the emulsion is called *emulsifier* or *emulsifying agent*. The commonly used emulsifying agents are soaps, detergents and lyophilic colloids. Casein, a lyophilic colloid present in milk, acts as an emulsifier as it forms a protective layer around fat molecules dispersed in water. Hence milk is a fairly stable emulsion.

**Function of emulsifier :** The main function of emulsifier or emulsifying agents is to lower the interfacial tension between oil and water and thus helps the intermixing of two liquids. For example, a molecule of a soap or detergent (emulsifier) gets concentrated at the interface between oil and water. The polar end of the emulsifier is in water and non-polar end is in oil as shown in figure. In a soap,  $\text{RCOONa}$ , R is the non-polar end, whereas  $\text{COO}^- \text{Na}^+$  is the polar end.

**Properties of emulsion :**

- (i) The size of particles of the dispersed phase of an emulsion is usually larger than in sols.
- (ii) Like colloidal particles, emulsions exhibit properties such as Tyndall effect, Brownian movement (provided the particles are not too large), electrophoresis, coagulation, etc.



**Demulsification :** The process which involves the breaking of an emulsion into two separate liquid layers is called demulsification. The following methods may be used to bring demulsification:

- (1) **Chemical Methods :** An emulsion may be demulsified by adding a chemical substance whose action on the dispersed phase and the dispersion medium is opposite to that of the original emulsifying agent used to produce the stable emulsion.
- (2) **Centrifugation :** Cream is separated from milk by the centrifugal method.
- (3) **Cooling :** Fat can be removed from milk by keeping it in a refrigerator for a few hours.

**Demulsification :**

Besides the above noted methods of demulsification, the following methods have also been developed :

- (i) Suitable centrifugal action-milk cream is separated from milk by centrifugation.
- (ii) Application of electric field-electrophoresis.
- (iii) Addition of an electrolyte having multivalent opposite charge than that on the dispersed phase.
- (iv) Chemical destruction of stabiliser.
- (v) Distilling off of one of the components, usually water.
- (vi) Addition of demulsifiers like alcohol, phenol etc.

**Oil in water type emulsion (O/W) Use of emulsion :**

- (1) Many pharmaceutical preparations-medicines, ointments, creams and various lotions are emulsions. It is believed that medicines are more effective and easily assimilated by the body tissues when they are in colloidal form i.e., emulsion.
- (2) All paints are emulsions.
- (3) The digestion of fat in the intestines is helped by emulsification. A little of the fat forms a medium soap (emulsifier) with the alkaline solution of the intestine and this soap emulsifies the rest of the fats, thus making it easier for the digestive enzymes to do their metabolic functions.
- (4) Soaps and detergents remove dust and dirt from the dirty piece of cloth by making an oil in water emulsion.
- (5) Milk is an emulsion of liquid fats in water.
- (6) In the process of metallurgy, one of the important steps is the concentration of ore which is usually done by froth floatation process in which an oil is added to the finely-divided ore taken in water. The particles of ore go on the surface due to formation of foams while the other impurities are left at the bottom of the vessel.
- (7) The emulsion of asphalt in water is used in road making and building.

**GELS**

Colloidal system in which liquids are the dispersed phase and solid act as the dispersion medium are called gels. The common examples are : boot polishes, jelly, gum arabic, agar agar, processed cheese and silicic acid.

When the gels are allowed to stand for a long time, they give out small quantities of trapped liquids which accumulate on its surface. This action of gels is known as Synresis or Weeping. Some gels such as silica, gelatin and ferric hydroxide liquify on shaking and reset on allowing to stand. This phenomenon of Sol-gel transformation is called thixotropy.

Gels are divided into two categories i.e. elastic gels and non elastic gels. The two categories differ from their behaviour towards dehydration and rehydration as under.

**Elastic gels**

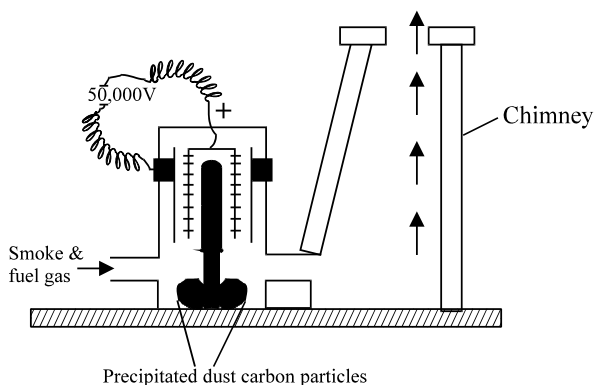
1. They change to solid mass on dehydration which can be changed back to original form by addition of water followed by warming.
2. They absorb water when placed in it with simultaneous swelling. This phenomenon is called imbibation.

**Non-elastic gels**

1. They change to solid mass on dehydration which cannot be changed back to original form with water.
2. They do not exhibit imbibation.

**USES OF COLLOIDS :**

- (1) **Medicines :** The medicines containing gold, silver or calcium etc. in colloidal form are more effective and easily assimilated by the human systems.
- (2) **Dyes :** In dyeing, mordants colloidal substances are used in textile dyeing industry to fasten dyes.
- (3) **Rubber industry :** Latex is a colloidal solution of negatively charged particles. The article to be rubber plated is made the anode. Under the influence of electric field the rubber particles get deposited on the anode and the article gets rubber plated.
- (4) **Smoke screens :** Smoke screens which consist of titanium dioxide dispersed in air are used in warfare for the purpose of concealment and camouflage.
- (5) **Formation of delta :** The river water carries with it charged clay particles and many other substances in the form of colloidal solution. When the sea water comes in contact with these particles, the colloidal particles in river water are coagulated by the electrolytes present in sea water to form deltas.
- (6) **Purification of water :** The turbidity in water is due to the presence of negatively charged clay particles. The addition of potash alum, i.e.,  $\text{Al}^{3+}$  ions neutralizes the negative charge on the colloidal particles and thus causes their coagulation. The coagulated matter settles down and thus becomes clear.
- (7) **Artificial rain :** Artificial rain can be caused by throwing electrified sand on clouds which are colloidal solutions or charged particles of water in air.
- (8) **Smoke precipitation :** Smoke coming out of the chimney in industrial area is a nuisance and health hazard. It is a colloidal particles are charged particles and thus they are removed from fuel gases by electrical precipitation (Cottrell Precipitator).



In cottrell precipitator, the smoke is made to pass through chambers fitted with highly electrically

charged plates which precipitate the carbon and dust particles leaving in the gases to escape through chimney (figure).

- (9) **Sewage disposal** : Sewage water consists of particles of dirt, rubbish, mud, etc., which are of colloidal dimensions and carry an electric charge and thus do not settle down easily. These particles can thus be removed by cataphoresis. A system of two tanks fitted with metallic electrodes is used for this purpose. When electric field is created, then the dust particles are coagulated on the oppositely charged electrodes. The deposit may be utilized as a manure.
- (10) **Cleansing action of soap and detergent** : Soap solution may be used to wash off the dirt sticking to the fabric, in the presence
- If it forms a colloidal solution in water forms (micelles), removes dirt by simple adsorption of oily substance and thus washes away.
  - It decreases the interfacial tension between water and grease, and it causes the emulsification of grease in water. By mechanical action such as rubbing, the dirt particles are also detached along with the oily material.
- (11) **In Photography** : Various colloidal systems are used in photographic process. In the preparation of photographic plates, the silver bromide in gelatin is coated on thin glass plates. In developing and fixation, various colloidal substances are used. In different kinds of colour printing, gelatin and other colloidal mixtures are used.
- (12) **Blue colour of the sky** : Colloidal particles scatter only blue light and the rest of it is absorbed. In sky there are a number of dust and water particles. They scatter blue light and, therefore, sky looks bluish. If there were no scattering, the sky would have appeared totally dark.

## **ADSORPTION**

This tendency of accumulation of molecular species at the surface than in the bulk of a solid (or liquid) is termed **adsorption**. The molecular species or substance which concentrates or accumulates at the surface is termed **adsorbate** and the material on whose surface the adsorption has taken place is called **adsorbent**.

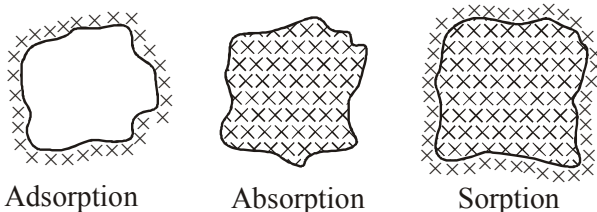
The reverse process i.e. removal of adsorbed substance from the surface is called **desorption**.

The adsorption of gases on the surface of metals is called **occlusion**.

The term **sorption** is employed when adsorption as well as absorption take place simultaneously.

### **DISTINCTION BETWEEN ADSORPTION AND ABSORPTION**

In adsorption the concentration of the adsorbate increases only at the surface of the adsorbent, while in absorption the concentration is uniform throughout the bulk of the solid.



Absorption is due to the fact that the surface particles of the adsorbent are in a different state than the particles inside the bulk. Inside the adsorbent all the forces acting between the particles are mutually balanced but on the surface the particles are not surrounded by atoms or molecules of their kind on all sides and hence they possess unbalanced or residual attractive forces. These forces of the adsorbent are responsible for attracting the adsorbate particle on its surface.

Adsorption is a surface phenomenon, whereas absorption is a bulk phenomenon. Adsorption occurs only at the surface of adsorbent, whereas absorption occurs throughout the body of the material.

ADSORPTION	ABSORPTION
1. It is a surface phenomenon.	1. It concerns with the whole mass of the absorbent.
2. In it, the substance is only retained on the surface and does not go into the bulk or interior of the solid or liquid	2. It implies that a substance is uniformly distributed, through the body of the solid or liquid
3. In it the concentration of the adsorbed molecules is always greater in the free phase.	3. In it the concentration is low
4. It is rapid in the beginning and slows down near the equilibrium.	4. It occurs at the uniform rate
5. Examples – (a) Water vapours adsorbed by silica gel, $\text{NH}_3$ is adsorbed by charcoal. (b) $\text{N}_2$ is adsorbed on mica, $\text{O}_2$ is adsorbed on tungsten surface	5. Examples (a) Water vapours absorbed by anhy. $\text{CaCl}_2$ (b) $\text{NH}_3$ is absorbed in water forming $\text{NH}_4\text{OH}$

### TYPES OF ADSORPTION

#### **(A) POSITIVE AND NEGATIVE ADSORPTION**

When the concentration of the adsorbate is more on the surface of the adsorbent than in the bulk, it is called positive adsorption.

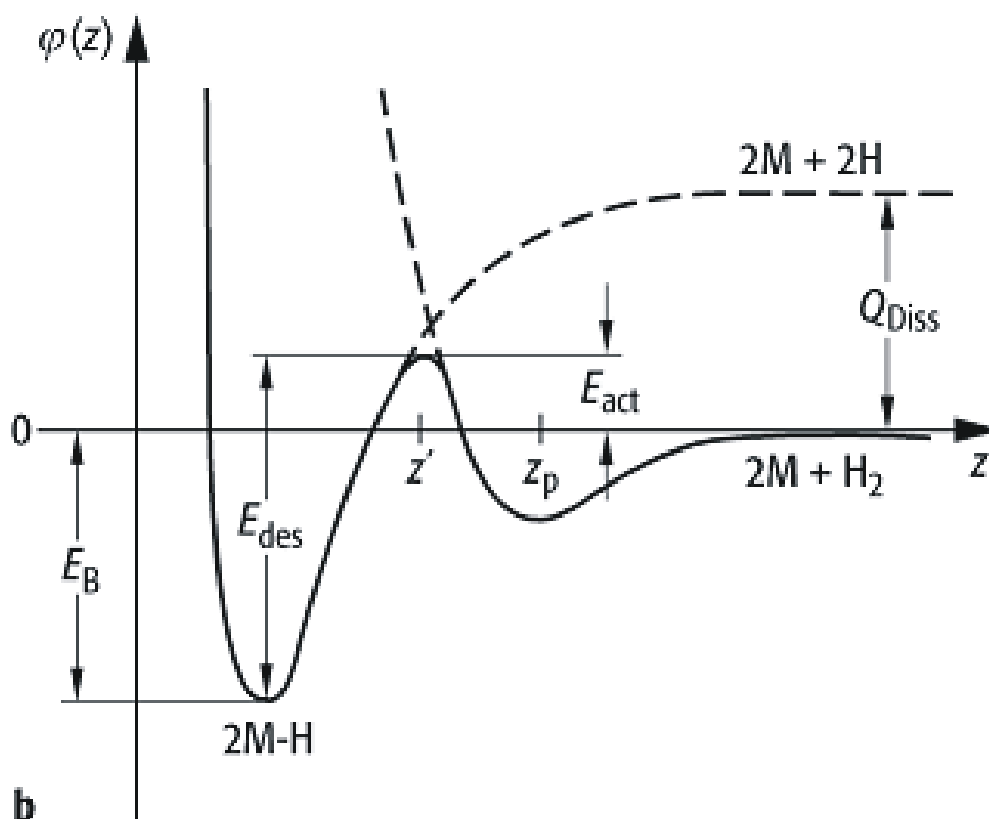
When the concentration of the adsorbate is less relative to its concentration in the bulk, it is called negative adsorption.

#### **(B) PHYSI-SORPTION AND CHEMISORPTION**

When a gas is adsorbed at the surface of a solid by weak forces (Vander Waal's forces), it is called **physical adsorption**.

When a gas is held on the surface of a solid by forces similar to those of a chemical bond, it is called **chemical adsorption or chemisorption**. The chemical bonds may be covalent or ionic in nature. Chemisorption has a rather high energy of activation and is, therefore, often referred to as activated adsorption.

Sometimes these two processes occur simultaneously and it is not easy to ascertain the type of adsorption. A physical adsorption at low temperature may pass into chemisorption as the temperature is increased. For example, hydrogen is first adsorbed on nickel by van der Waals' force. Molecules of hydrogen then dissociate and hydrogen atoms are held on the surface by chemisorption.

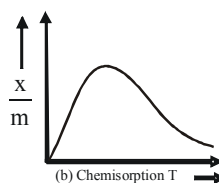
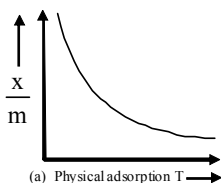
**POTENTIAL ENERGY MAPE OF PHYSI-SORPTION AND CHEMISORPTION****COMPARISON OF PHYSI-SORPTION AND CHEMISORPTION****Physical adsorption**

1. It is caused by intermolecular van der Waals' forces.
2. It is not specific.
3. It is reversible.
4. It depends on the nature of gas. More easily which form com liquefiable gases are adsorbed readily.
5. Heat of adsorption is low.
6. Low temperature is favourable. It decreases increase with increase of temperature.

**Chemical adsorption**

- It is caused by chemical bond formation.
- It is highly specific.
- It is irreversible.
- It depends on the nature of gas. Gases pounds with the adsorbent exhibit chemi-sorption.
- Heat of adsorption is high.
- High temperature is favourable. It increases with of temperature.





- |  |   |
|--|---|
| 7. No appreciable activation energy is involved.                               | High activation energy is involved.   |
| 8. High pressure is favourable. Decrease of pressure causes desorption.        | High pressure is favourable. Decrease of pressure not cause desorption.     |
| 9. It depends on the surface area. It increases with increase of surface area. | It also depends on the surface area. It increases increase of surface area. |
| 10. It forms multilayers on adsorbent surface under high pressure.             | It forms unimolecular layer.  |

### **CHARACTERSTIC OF ADSORPTION**

Molecules at the surface of a solid, a metal, or a liquid experience in net inward force of attraction with free valencies.

Adsorption is accompanied by evolution of heat. The amount of heat evolved when one mole of a gas is adsorbed on a solid, is known as molar heat of adsorption. Its magnitude depends upon the nature of the gas.

The magnitude of gaseous adsorption depends upon temperature, pressure, nature of the gas and the nature of the adsorbent.

Adsorption decreases with increase in temperature, since it is accompanied by evolution of heat.

The adsorption increases with increase in pressure, since adsorption of gas leads to decrease in pressure.

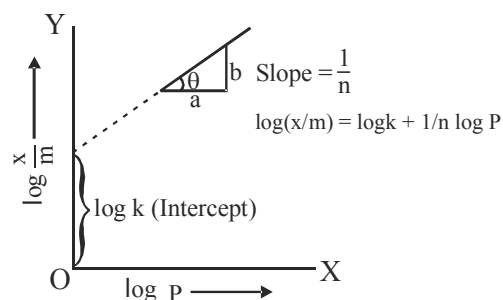
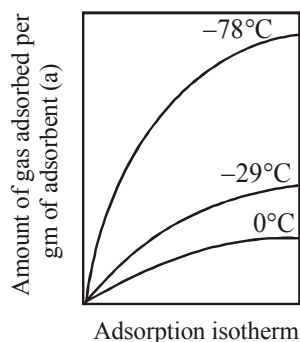
More readily soluble and easily liquefiable gases  $\text{HCl}$ ,  $\text{Cl}_2$ ,  $\text{SO}_2$  and  $\text{NH}_3$  are adsorbed more than the so called permanent gases such as  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$  etc. because Vander Waal's forces involved in adsorption are much predominant in the former gases than the latter category of gases.

### **ADSORPTION ISOTHERM**

The variation of adsorption with pressure at a constant temperature is called adsorption isotherm.

#### **(1) FREUNDLICH ADSORPTION ISOTHERM**

Freundlich, in 1909, gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. The relationship can be expressed by the following equation.



At constant temperature  $x/m = k \cdot P^{1/n}$

where 'x' is the mass of the gas adsorbed on a mass 'm' of the adsorbent at a pressure P. k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature.

At low pressure, the amount of the gas adsorbed per unit quantity of adsorbent is proportional to the pressure. At high pressure, the amount of adsorbed gas is independent of pressure. At intermediate pressures, Freundlich adsorption isotherm is expected to hold

## 2 LANGMUIR ADSORPTION ISOTHERM:-

According to Langmuir —

- (a) There is adsorption of gas molecules on the surface of the solid.
- (b) There is desorption of the adsorbed molecules from the surface of the solid.
- (c) There is formation of unimolecular layer and thus it is chemisorption
- (e) A dynamic equilibrium is attained when rate of adsorption = rate of desorption.
- (f) Based on the above facts, langmuir adsorption isotherm is represented as

$$\theta = \frac{aP}{1 + bP}, \text{ (where } \theta \text{ is fractional coverage)}$$

**Case-I** At very high pressure

$$bP \gg 1, \text{ hence } 1 + bP \approx bP$$

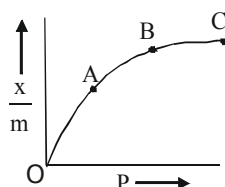
$$\therefore \theta = \frac{aP}{bP} = \frac{a}{b} = \text{constant}$$

This shows saturation point as shown along BC.

**Case-II** At very low pressure

$$bP \ll 1 \therefore 1 + bP \approx 1 \quad \therefore \theta = aP, \quad \Rightarrow \theta \propto P$$

This is shown along OA



**SOLVED EXAMPLE**

**Ex.1** The charge on the colloidal particle of soap in its solution developed -

- (A) By preferential adsorption of ions
- (B) The effective ion of soap micelle carries negative charge
- (C) The effective ion of soap micelle carries positive charge
- (D) None of the above

**Sol. B**



The active species of soap is negatively charged.

**Ex.2** In order to coagulate the impurities present in water. Which is the most effective ion present in the 'alum' -

- (A)  $\text{K}^+$
- (B)  $\text{SO}_4^{2-}$
- (C)  $\text{Al}^{3+}$
- (D) None of these

**Sol. C**

The impurities carry negative charge hence  $\text{Al}^{3+}$  will exhibit maximum coagulating power.

**Ex.3** Which is not the property of the hydrophilic sols-

- (A) High concentration of dispersed phase can be easily attained
- (B) Coagulation is reversible
- (C) The charge of the particle depends upon the pH values of the dispersion medium. It may be positive or negative
- (D) Viscosity and that surface tension are about the same as of dispersion medium.

**Sol. D**

Viscosity of hydrophilic sol is much higher than dispersion medium while surface tension of the sol is much lesser than water. This is attributed to the higher concentration of the sol itself.

**Ex.4** If water is chosen as dispersion medium, then the sol formed will be called -

- (A) Alcoholsol
- (B) Benzosol
- (C) Hydrosol
- (D) Aerosol

**Sol. C**

If water is chosen as dispersion medium then the colloidal system will be called hydrosol.

**Ex.5** The number of moles of lead nitrate needed to coagulate 2 mole of colloidal  $[\text{AgI}]\text{I}^-$  is-

- (A) 2
- (B) 1
- (C)  $\frac{1}{2}$
- (D)  $\frac{2}{3}$

**Sol.**  $2[\text{AgI}]\text{I}^- + \text{Pb}^{2+} \rightarrow \text{PbI}_2 + 2\text{AgI}$

Thus, one mole of  $\text{Pb}(\text{NO}_3)_2$  is required to coagulate 2 mole of  $[\text{AgI}]\text{I}^-$ .

**Ex.6** Maximum hydrophobic character will be shown by

- (A) Glycine
- (B) Stearic acid
- (C) Glucose
- (D) Adenine

**Sol. D**

Adenine exhibits maximum hydrophobic character.

**Ex.7**  $\text{Fe}(\text{OH})_3$  sol obtained by peptization when subjected to 'electrophoretic effect' -

- (A) Colloidal particles will migrate towards anode
- (B) Colloidal particles will migrate towards cathode
- (C) Colloidal particles remain stationary
- (D) Colloidal particles migrate towards both the electrode

**Sol. B**

Ferric hydroxide is a positive sol  $\text{Fe}(\text{OH})_3/\text{Fe}^{3+}$ , it will migrate towards cathode.

**Ex.8** Which of the following solution is positively charged -

- (A)  $As_2S_3$  (B)  $Fe(OH)_3$  (C) Au (D) Starch

**Sol. B**

$Fe(OH)_3/Fe^{3+}$  is a positively sol particle.

**Ex.9** Dispersion of AgCl in water is called -

- (A) Hydrophilic sol (B) Emulsion (C) Benzosol (D)Hydrophobic colloid

**Sol. D**

Colloidal system AgCl is called, hydrophobic colloid.

**Ex.10** The stability of lyophilic colloid is due to -

- (A) Charge on the solution particles (B) Layer of dispersion medium over the solution particles  
(C) Smaller size of solution particles (D) Bigger size of solution particles

**Sol. B**

Lyophilic colloids are of bigger size and this accounts for their stability.

**Ex.11** The volume of nitrogen gas at  $0^\circ C$  and 1.013 bar required to cover a sample of silica gel with unimolecular layer is  $129 \text{ cm}^3 \text{ g}^{-1}$  of gel. Calculate the surface area per gram of the gel if each nitrogen molecule occupies  $16.2 \times 10^{-20} \text{ m}^2$ .

**Sol.  $568 \text{ m}^2 \text{ g}^{-1}$**

$$PV = nRT$$

$$1.013 \times 0.129 = n \times 0.0821 \times 273$$

$$n = 0.00583 \text{ mol}$$

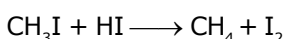
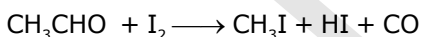
Area occupied

$$= 0.00583 \times 6.023 \times 10^{23} \times 16.2 \times 10^{-20}$$

**Ex.12** The rate of decomposition of acetaldehyde into methane and CO in the presence of  $I_2$  at 800 K follows the rate law

$$\text{Rate} = k[\text{CH}_3\text{CHO}][I_2]$$

The decomposition is believed to go by the two steps mechanism



What is the catalyst for the reaction ? Which of the two steps is a slower one ?

**Sol.**  $I_2$  is catalyst ; first step is slow.

**Ex.13** A catalyst lowered the activation energy by 25 kJ/mol at  $25^\circ C$ . By how many times will the rate slow ?

**Sol. 24069 times**

$$\frac{K_p}{K_a} = \text{Antilog} \left[ \frac{\Delta E}{2.303 RT} \right]$$

$$= \text{Antilog} \left[ \frac{25 \times 10^3}{2.303 \times 8.314 \times 298} \right] = 24069 \text{ times}$$

**Ex.14** Discuss the effect of temperature on the degree of adsorption of  $N_2$  on the surface of iron.

**Sol.** At room temperature, practically there is no adsorption of  $N_2$  gas on the surface of iron. At 83 K, nitrogen is physically adsorbed on the surface of iron. Its degree of adsorption decreases with rise in temperature and becomes almost nil at room temperature. At 773 K and above, there is chemical adsorption of nitrogen on the surface of iron.

**Ex.15** One gram of charcoal adsorbs 100 mL of 0.5 M  $\text{CH}_3\text{COOH}$  to form a mono-layer and thereby the molarity of acetic acid is reduced to 0.49 M. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal =  $3.01 \times 10^2 \text{ m}^2/\text{gm}$ .

**Sol.** Number of moles of acetic acid initially present =  $\frac{MV}{1000} = \frac{0.5 \times 100}{1000} = 0.05$

Number of moles of acetic acid left =  $\frac{MV}{1000} = \frac{0.49 \times 100}{1000} = 0.049$

Number of moles of acetic acid adsorbed =  $0.05 - 0.049 = 0.001 \text{ mol}$

Number of molecules of acid adsorbed =  $0.001 \times 6.023 \times 10^{23} = 6.023 \times 10^{20}$

Area occupied by single molecule of acetic acid =  $\frac{\text{Total area}}{\text{Number of molecules adsorbed}}$

$$= \frac{3.01 \times 10^2}{6.023 \times 10^{20}} = 5 \times 10^{-19} \text{ m}^2$$

**Ex.16**  $1.30 \text{ cm}^3$  of  $\text{N}_2$  gas at STP is adsorbed per gram of silica gel. The area occupied by nitrogen molecule is  $0.16 \text{ nm}^2$ . What is the surface area per gram of silica gel ?

( $N_A = 6.023 \times 10^{23}$ )

(A)  $1.6 \text{ m}^2 \text{ g}^{-1}$  (B)  $5.568 \text{ m}^2 \text{ g}^{-1}$  (C)  $3.48 \text{ m}^2 \text{ g}^{-1}$  (D)  $4.42 \text{ m}^2 \text{ g}^{-1}$

**Sol. B**

Number of  $\text{N}_2$  molecules adsorbed per gram of silica gel

$$= \frac{1.30 \times 6 \times 10^{23}}{22400} = 3.48 \times 10^{19}$$

Area of cross-section of molecule =  $0.16 \text{ nm}^2$

$$= 1.6 \times 10^{-19} \text{ m}^2$$

Surface area covered per gram of silica gel

$$= 1.6 \times 10^{-19} \times 3.48 \times 10^{19} = 5.568 \text{ m}^2$$

**Ex.17** Plot of  $\log \left( \frac{x}{m} \right)$  against  $\log P$  is a straight line inclined at an angle of  $45^\circ$ . When the pressure is 0.5 atm and Freundlich parameter,  $k$  is 10, the amount of solute adsorbed per gram of adsorbent will be : ( $\log 5 = 0.6990$ )

(A) 1 g (B) 2g (C) 3 g (D) 5 g

**Sol. D**

$$\log \left( \frac{x}{m} \right) = \log k + \frac{1}{n} \log P$$

$$\frac{1}{n} = \tan 45^\circ = 1$$

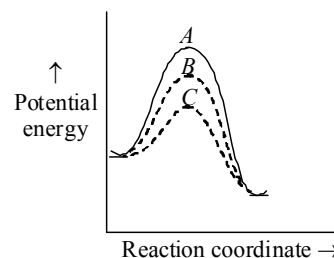
$$\log k = \log 10 = 1$$

$$\frac{x}{m} = k(P)^{1/n} = 10(0.5)^1 = 5$$

When  $m = 1 \text{ g}$ ,  $x = 5 \text{ g}$

**Ex.18** In homogeneous catalytic reactions, there are three alternative paths A, B and C (shown in the figure). Which one of the following indicates the relative case with which the reaction can take place ?

- (A)  $A > B > C$                       (B)  $C > B > A$   
 (C)  $B > C > A$                       (D)  $A = B = C$



**Sol.** Activation energy in the different paths lies in the following sequence :  $C < B < A$ .  
 Lesser is the activation energy, greater is the ease with which the reaction can take place.  
 $\therefore C > B > A$  (Decreasing case with which the reaction can take place.)

**Ex.19** The coagulation of 100 mL of a colloidal solution of gold is completely prevented by adding 0.25 g of starch to it before adding 10 mL of 10% NaCl solution. Find out the gold number of starch.

**Sol.** 10 mL of 10% NaCl solution is added to 100 mL of solution of gold.  
 Thus, 1 mL of 10% NaCl solution has been added to 10 mL solution of gold.  
 Since, 100 mL gold solution required = 0.25 g starch  
 $= 0.25 \times 10^3$  mg starch  
 So, 10 mL gold solution required

$$= \frac{0.25 \times 10^3}{100} \times 10$$

$$= 25 \text{ mg starch}$$

Thus, by definition, the gold number of starch is 25.

**Ex.20** The coagulation of 100 mL of colloidal solution of gold is completely prevented by addition of 0.25 g of a substance "X" to it before addition of 1 mL of 10 % NaCl solution. The gold number of "X" is-

- (A) 0.25                      (B) 25                      (C) 250                      (D) 2.5

**Sol.** Number of milligrams of protective colloid added in 10 mL of colloidal gold to prevent its coagulation on addition of 1 mL of 10% NaCl solution is called its gold number.  
 $\therefore$  Gold number of present colloid = 25

## Discussion Questions

- (1) How will you differentiate between a true solution and a colloidal dispersion?
- (2) Identify some sols (colloids) that you use in your daily life and mention their importance.
- (3) How do colloids acquire a charge? Why is ferric hydroxide/aluminium hydroxide sol prepared in the experiment, positively charged while arsenious sulphide sol is negatively charged?
- (4) What is coagulation? How is coagulation different from peptization?
- (5) How can you convert a colloidal dispersion of sulphur into a true solution?
- (6) Out of lyophilic and lyophobic sols, which one can be easily converted into a gel and why?
- (7) Differentiate between a gel and a sol.
- (8) What are the applications of colloids in the field of Medicine, Defense and in Rocket Technology?
- (9) How can you make the process of dialysis quick? What are the limitations of this technique?
- (10) Name a reagent other than soap, which can be used as an emulsifying agent in the oil in water type emulsion.
- (11) Milk is said to be a stable emulsion. What provides stability to milk?
- (12) Can two miscible liquids form an emulsion?
- (13) Why do separation of layers of different oils forming an emulsion with water take different time?
- (14) What are the points of similarity and dissimilarity among sol, gel and emulsion?
- (15) Suggest a test to distinguish between Oil in Water and Water in Oil type of emulsions.
- (16) Give some examples of emulsions that you come across in daily life.
- (17) Dettol forms an emulsion in water. How does this emulsion get stabilised?

**PROFICIENCY TEST****Fill in the blanks with appropriate items :**

1. The substance on whose surface adsorption takes place is called an \_\_\_\_\_ .
2. Removal of adsorbate from the surface of adsorbent is called \_\_\_\_\_ .
3. Migration of colloidal particles under the effect of electric field is called \_\_\_\_\_ .
4. The heat of adsorption in case of physisorption is approximately \_\_\_\_\_ .
5. The phenomenon of zig-zag motion of colloidal particles is known as \_\_\_\_\_ .
6. Lyophilic sols are \_\_\_\_\_ stable than lyophobic sols.
7. Electrical properties of a colloidal solution are demonstrated by \_\_\_\_\_ .
8. Tyndall effect takes place due to \_\_\_\_\_ of light by colloidal particles.
9. The liquid-liquid colloidal dispersions are called \_\_\_\_\_ .
10. The movement of dispersion medium under the influence of an electric field is called \_\_\_\_\_ .
11. Smoke is a colloidal solution of \_\_\_\_\_ in \_\_\_\_\_ .
12. The adhering of the molecules of a gas on the surface of a solid is called \_\_\_\_\_ .
13. The protective action of different colloids is compared in terms of \_\_\_\_\_ .
14. The colloidal dispersion of a liquid in a liquid is called \_\_\_\_\_ .
15. The colloidal dispersions of liquids in solid media are called \_\_\_\_\_ .

**True / False statements :**

1. Physisorption is non-specific.
2. Chemisorption needs activation energy.
3. A graph of  $x/m$  vs temperature at constant pressure is called adsorption isotherm.
4. Suspensions have solute particles with size less than 1 nm.
5.  $\text{Fe}(\text{OH})_3$  sol contains positively charged colloidal particles.
6. Chemisorption is irreversible.
7. Adsorption isobars of chemisorption and physisorption are of the same type.
8. Milk is an example of water in oil emulsions.
9. Gold sol can be prepared by Bredig's arc method.
10. Gel is a system in which liquid is the dispersed phase and solid is the dispersion medium.

**EXERCISE – I****OBJECTIVE PROBLEMS (JEE MAIN)**

1. Which gas will be adsorbed on a solid to greater extent.  
 (A) A gas having non polar molecule  
 (B) A gas having highest critical temperature ( $T_c$ )  
 (C) A gas having lowest critical temperature.  
 (D) A gas having highest critical pressure.

**Sol.**

2. Which of the following factors affects the adsorption of a gas on solid ?  
 (A)  $T_c$  (critical temp.)  
 (B) Temperature of gas  
 (C) Pressure of gas  
 (D) All of them

**Sol.**

3. The volume of gases  $\text{NH}_3$ ,  $\text{CO}_2$  and  $\text{CH}_4$  adsorbed by one gram of charcoal at 298 K are in  
 (A)  $\text{CH}_4 > \text{CO}_2 > \text{NH}_3$   
 (B)  $\text{NH}_3 > \text{CH}_4 > \text{CO}_2$   
 (C)  $\text{NH}_3 > \text{CO}_2 > \text{CH}_4$  (D)  $\text{CO}_2 > \text{NH}_3 > \text{CH}_4$

**Sol.**

4. The heat of physisorption lie in the range of  
 (A)  $1 - 10 \text{ kJ mol}^{-1}$   
 (B)  $20 \text{ to } 40 \text{ kJ mol}^{-1}$   
 (C)  $40 \text{ to } 200 \text{ kJ mol}^{-1}$   
 (D)  $200 \text{ to } 400 \text{ kJ mol}^{-1}$

**Sol.**

5. Which of the following is not a gel ?  
 (A) Cheese (B) Jellies  
 (C) Curd (D) Milk

**Sol.**

6. Which of the following is used to adsorb water  
 (A) Silica gel (B) Calcium acetate  
 (C) Hair gel (D) Cheese

7. An emulsion is colloidal system of  
 (A) two solids  
 (B) two liquids  
 (C) one gas and one solid  
 (D) one gas and one liquid

**Sol.**

8. Which of the following is a lyophobic colloid ?  
 (A) Gelatin (B) Sulphur  
 (C) Starch (D) Gum arabic

**Sol.**

9. The nature of bonding forces in adsorption  
 (A) purely physical such as Van Der Waal's forces  
 (B) purely chemical  
 (C) both chemical and physical always  
 (D) none of these

**Sol.**

10. The Tyndall effect associated with colloidal particles is due to  
 (A) presence of electrical charges  
 (B) scattering of light  
 (C) absorption of light  
 (D) reflection of light

**Sol.**

11. Which one of the following is not applicable to chemisorption ?  
 (A) Its heat of adsorption is high  
 (B) It takes place at high temperature  
 (C) It is reversible  
 (D) It forms mono-molecular layers

**Sol.**



12. In the colloidal state the particle size ranges  
(A) below 1 nm  
(B) between 1 nm to 1000 nm  
(C) more than 100 nm  
(D) none of the above

**Sol.**

13. All colloids  
(A) are suspensions of one phase in another  
(B) are two-phase systems  
(C) contain only water soluble particles  
(D) are true solutions

**Sol.**

14. Colloids can be purified by  
(A) condensation (B) peptization  
(C) coagulation (D) dialysis

**Sol.**

15. Milk is an example of  
(A) emulsion (B) suspension  
(C) foam (D) sol.

**Sol.**

16. Colloidal particles in a sol. can be coagulated by  
(A) heating  
(B) adding an electrolyte  
(C) adding oppositely charged sol  
(D) any of the above methods

**Sol.**

17. Fog is a colloidal system of  
(A) gas in liquid (B) liquid in gas  
(C) gas in gas (D) gas in solid

**Sol.**

18. Given below are a few electrolytes, indicates which one among them will bring about the coagulation of a gold sol. quickest and in the least of concentration ?  
(A) NaCl (B)  $\text{MgSO}_4$   
(C)  $\text{Al}_2(\text{SO}_4)_3$  (D)  $\text{K}_4[\text{Fe}(\text{CN})_6]$

**Sol.**

19. When a colloidal solution is observed under ultramicroscope, we can see  
(A) light scattered by colloidal particle  
(B) size of the colloidal particle  
(C) shape of the colloidal particle  
(D) relative size of the colloidal particle

**Sol.**

20. Colloidal solution are classified on the basis of  
(A) molecules size  
(B) organic or inorganic  
(C) surface tension value  
(D) pH value

**Sol.**

21. The electrical charge on a colloidal particle is indicated by  
(A) Brownian movement  
(B) electrophoresis  
(C) ultra microscope  
(D) molecular sieves

**Sol.**

22. The minimum concentration of an electrolyte required to cause coagulation of a sol. is called  
(A) flocculation value (B) gold number  
(C) protective value (D) none of these

**Sol.**

23. Smoke precipitator works on the principle of  
(A) distribution law  
(B) neutralization of charge on colloids  
(C) Le-Chateliers principle  
(D) addition of electrolytes

**Sol.**

24. Which one of following statement is not correct in respect of lyophilic sols ?  
(A) There is a considerable interaction between the dispersed phase and dispersion medium  
(B) These are quite stable and are not easily coagulated  
(C) They carry charge  
(D) The particle are hydrated

**Sol.**

25.  $\text{As}_2\text{S}_3$  sol is  
(A) positive colloid (B) negative colloid  
(C) neutral colloid (D) none of the above

**Sol.**

26. Crystalloids differ from colloids mainly in respect of  
(A) electrical behaviour  
(B) particle nature  
(C) particle size  
(D) solubility

**Sol.**

27. At the critical micelle concentration (CMC) the surfactant molecules  
(A) decompose  
(B) dissociate  
(C) associate  
(D) become completely soluble

**Sol.**

28. Alums purify muddy water by  
(A) dialysis  
(B) absorption  
(C) coagulation  
(D) forming true solution

**Sol.**

29. Solute dispersed in ethanol is called  
(A) emulsion (B) micelle  
(C) hydrophilic sol.  
(D) alcosols

**Sol.**

30. Which one of the following is lyophilic colloid ?  
(A) Milk (B) Gum  
(C) Fog (D) Blood

**Sol.**

31. Small liquid droplets dispersed in another liquid is called  
(A) suspension (B) emulsion  
(C) gel (D) true solution

**Sol.**

32. The process which is catalysed by one of the product is called  
(A) acid-base catalysis  
(B) autocatalysis  
(C) negative catalysis  
(D) homogeneous catalysis

**Sol.**

33. Tyndall effect would be observed in a  
(A) solution (B) solvent  
(C) precipitate (D) colloidal sol.

**Sol.**

34. Adsorption is multilayer in case of  
(A) physical adsorption  
(B) chemisorption  
(C) in both  
(D) none of the these

**Sol.**

35. A liquid is found to scatter a beam of light but leaves no residue when passed through the filter paper. The liquid can be described as  
(A) a suspension (B) oil  
(C) a colloidal sol. (D) a true solution

**Sol.**

**EXERCISE – II****OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. The ability of an ion to bring about coagulation of a given colloid depends upon

(A) its charge  
(B) the sign of the charge alone  
(C) the magnitude of the charge  
(D) both magnitude and sign of charge

**Sol.**

2. An arsenious sulphide sol. carries a negative charge. The maximum precipitating power of this sol. is possessed by

(A)  $K_4[Fe(CN)_6]$  (B)  $CaCl_2$   
(C)  $Na_3PO_4$  (D)  $AlCl_3$

**Sol.**

3. Reversible adsorption is  
(A) chemical adsorption  
(B) physical adsorption  
(C) both  
(D) none

**Sol.**

4. Which of the following is an example of associated colloid ?

(A) Protein + water  
(B) Soap + water  
(C) Rubber + benzene  
(D)  $As_2O_3 + Fe(OH)_3$

**Sol.**

5. Adsorption of gases on solid surface is generally exothermic because

(A) enthalpy is positive  
(B) entropy decreases  
(C) entropy increases  
(D) free energy increases

**Sol.**

6. An emulsifier is a substance  
(A) which stabilises an emulsion  
(B) which breaks the emulsion into its constituent liquids  
(C) which can convert liquid into an emulsion  
(D) which brings about coagulation of an emulsion

**Sol.****Question No. 7 to 9 (3 questions)**

Whenever a mixture of gases is allowed to come in contact with a particular adsorbent under the same conditions, the more strong adsorbate is adsorbed to greater extent irrespective of its amount present, e.g.  $H_2O$  is adsorbed to more extent on silica gel than  $N_2$  and  $O_2$ . This shows that some adsorbates are preferentially adsorbed. It is also observed that preferentially adsorbable adsorbent can displace a weakly adsorbed substance from the surface of an adsorbent.

7. Which of the gas can displace remaining all the gases.

(A)  $O_2$  (B)  $N_2$   
(C)  $CO$  (D)  $H_2$

**Sol.**

8. When temperature is increased  
(A) extent of adsorption increases  
(B) extent of physical adsorption decreases  
(C) no effect on adsorption  
(D) extent of physical adsorption first decreases, then increases

Sol.

9. Activated charcoal is prepared by
- heated charcoal with steam so that it becomes more porous
  - adding  $\text{Ca}_3(\text{PO}_4)_2$  to charcoal
  - adding impurity to charcoal
  - reacted with conc.  $\text{HNO}_3$

Sol.

**Question No. 10 to 12 (3 questions)**

The clouds consist of charged particles of water dispersed in air. Some of them are +vely charged, others are negatively charged. When +vely charged clouds come closer they have cause lightening and thundering whereas when +ve and -ve charged colloids closer they cause heavy rain by aggregation of minute particles. It is possible to cause artificial rain by throwing electrified sand or silver iodide from an aeroplane and thus coagulation the mist hanging in air.

10. When excess of  $\text{AgNO}_3$  is treated with KI solution, AgI forms
- +ve charged sol
  - ve charged sol
  - neutral sol
  - true solution

Sol.

11. Clouds are colloids solution of
- liquid in gas
  - gas in liquid
  - liquid in liquid
  - solid in liquid

Sol.

12. Electrical chimneys are made on the principle of
- Electroosmosis
  - Electrophoresis
  - Coagulation
  - All of these

Sol.

**Question No. 13 to 17 (5 questions)**

In macromolecular type of colloids, the dispersed particles are themselves large molecules (usually polymers). Since these molecules have dimensions comparable to those of colloidal particles, their dispersions are called macromolecular colloids. Most lyophilic sols belong to this category. These are certain colloids which behave as normal strong electrolytes at low concentrations, but exhibit colloidal properties at higher concentrations due to the formation of aggregated particles. These are known as micelles or associated colloids. Surface active agents like soaps and synthetic detergents belong to this class.

Critical micelle concentration (CMC) is the lowest concentration at which micelle formation appears. CMC increases with the total surfactant concentration. At concentration higher than CMC, they form extended parallel sheets known as **lamellar micelles** which resemble biological membranes. With two molecules thick, the individual molecule is perpendicular to the sheets such that hydrophilic groups are on the outside in aqueous solution and on the inside is a non-polar medium.

In concentrated solution, micelles take the form of long cylinders packed in hexagonal arrays and are called lyotropic mesomorphs.

In an aqueous solution (polar medium), the polar group points towards the periphery and the hydrophobic hydrocarbon chains point towards the conforming the core of the micelle.

Micelles from the ionic surfactants can be formed only above a certain temperature called the **Kraft temperature**.

They are capable of forming ions

Molecules of soaps and detergents consist of lyophilic as well as lyophobic parts which associate together to form micelles.

Micelles may contain as many as 100 molecules or more.

13. Surfactant molecules can cluster together as micelles, which are colloid sized cluster of molecules. Micelles form only above critical micelle concentration (CMC) and above certain temperature called kraft temperature. Which is false about micelle formation ?

(A)  $\Delta S$  of micelle formation is positive  
 (B) the hydrophobic part lie towards interior of micelle in water  
 (C) the hydrophilic part lie towards surface of micelle in water  
 (D)  $\Delta S$  of micelle formation is negative

**Sol.**

14. Select incorrect statement(s) :
- (A) Surface active agent like soaps and synthetic detergents can form micelles  
 (B) Soaps may act as emulsifying agents  
 (C)  $C_{17}H_{35}$  (hydrocarbon part) and  $-COO^-$  (carboxylate) part of stearate ion ( $C_{17}H_{35}COO^-$ ) both are hydrophobic  
 (D) All are incorrect statements

**Sol.**

15. Which part of the soap ( $RCOO^-$ ) dissolves greases and forms micelle ?
- (A) R part (called tail of the anion)  
 (B)  $-COO^-$  part (called head of the anion)  
 (C) both (A) and (B)  
 (D) none of these

**Sol.**

16. In multimolecular colloidal sols, atoms or molecules are held together by :
- (A) H-bonding  
 (B) van der Waals forces  
 (C) ionic bonding  
 (D) polar covalent bonding

**Sol.**

17. Cleansing action of soap occurs because :
- (A) oil and greases can be absorbed into the hydrophobic centres of soap micelles and washed away  
 (B) oil and grease can be absorbed into hydrophilic centres of soap micelles and washed away  
 (C) oil and grease can be absorbed into both hydrophilic and hydrophobic centres but not washed away  
 (D) cleansing action is not related to micelles

**Sol.**

### Question No. 18 to 20 (3 questions)

The protective power of the lyophilic colloids is expressed in terms of gold number a term introduced by Zsigmondy Gold number is the number of milligram of the protective colloid which prevent the coagulation of 10 ml of red gold sol, when 1 ml of a 10 percent solution of sodium chloride is added to it. Thus, smaller the gold number of lyophilic colloid, the greater is the protective power.

18. On addition of one mL of solution of 10% NaCl to 10 mL of red gold sol in presence of 0.025 g of starch, the coagulation is just prevented. The gold number of starch is
- (A) 0.025                      (B) 0.25  
 (C) 2.5                         (D) 25

**Sol.**

19. Which of the following statement(s) is/are correct
- (A) Higher the gold number, more to the protective power of colloid  
 (B) Lower the gold number, more the protective power  
 (C) Higher the coagulation value, more the coagulation power  
 (D) Lower the coagulation value, higher the coagulation power

Sol.

20. Gold number gives an indication of
- protective nature of colloids
  - purity of gold in suspension
  - the charge on a colloidal solution of gold
  - g-mole of gold per litre

Sol.

**Question No. 21 to 25 (5 questions)**

These questions consist of two statement each, printed as assertion and reason, while answering these questions you are required to choose any one of the following responses.

- If assertion is true but the reason is false.
- If assertion is false but the reason is true.
- If both assertion and reason are true and the reason is a correct explanation of assertion
- If both assertion and reason are true but reason is not a correct explanation of assertion.

21. **Assertion :** Isoelectric point is pH at which colloidal can move towards either of electrode  
**Reason :** At isoelectric point, colloidal particles become electrically neutral.

Sol.

22. **Assertion :** When  $\text{AgNO}_3$  is treated with excess of potassium iodide, colloidal particles gets attracted towards anode.  
**Reason :** Precipitate adsorb common ion (excess) and thus become charged.

Sol.

23. **Assertion :** For adsorption  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  all have -ve values

**Reason :** Adsorption is a spontaneous exothermic process in which randomness decreases due to force of attraction between adsorbent and adsorbate.

Sol.

24. **Assertion :** A gas with higher critical temperature gets adsorbed to more extent than a gas with lower critical temperature.

**Reason :** The easily liquifiable gases get adsorbed to more extent.

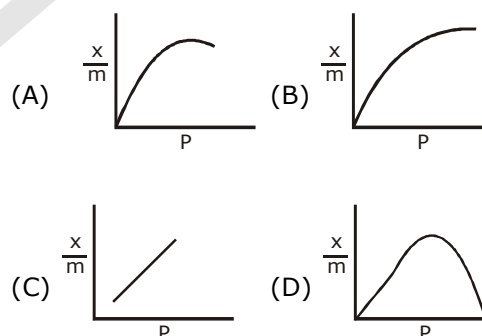
Sol.

25. **Assertion :** Physical adsorption of molecules on the surface requires activation energy.

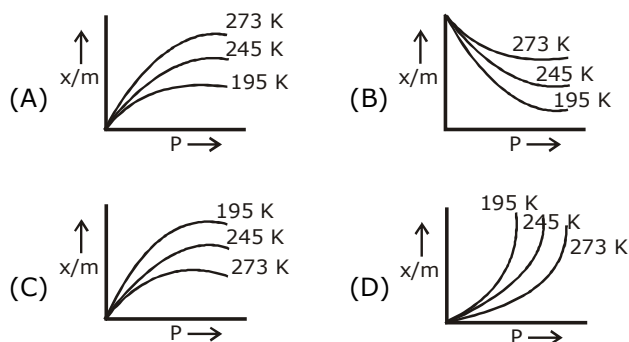
**Reason :** Heat of adsorption is -ve.

Sol.

26. The plot representing adsorption isotherm is



Sol.



Sol.

Select the correct alternative.

(More than one are correct)

28. Which of the following is/are correct statements

- (A) Hardy Schulz rule is related to coagulation
- (B) Brownian movement and Tyndall effect are shown by colloids
- (C) When liquid is dispersed in liquid, it is called gel.
- (D) Gold number is a measure of protective power of lyophilic colloid

Sol.

29. Which statement(s) is /are correct ?

- (A) Physical adsorption is multilayer non-directional and non specific
- (B) Chemical adsorption is generally monolayer and specific in nature
- (C) Physical adsorption is due to free valence of atoms
- (D) Chemical adsorption is stronger than physical adsorption

Sol.

30. Which of the following is/are correct for aq. lyophilic sols ?

- (A) Its surface tension is lower than that of  $H_2O$
- (B) Its viscosity is higher than that of water
- (C) Its surface tension is higher than that of water
- (D) Its viscosity is equal to that of water

Sol.

31. Which statement(s) is /are correct

- (A) A solution is prepared by addition of excess of  $AgNO_3$  solution in KI solution. The charge likely to develop on colloidal particle is positive
- (B) The effects of pressure on physical adsorption is high if temperature is low
- (C) Ultracentrifugation process is used for preparation of lyophobic colloids.
- (D) Gold number is the index for extent of gold plating done.

Sol.

32. Colloidal solution can be purified by

- (A) Dialysis (B) Electrodialysis
- (C) Electrophoresis (D) Ultrafiltration

Sol.

33. Coagulation of colloids can be achieved by

- (A) Centrifugation (B) Adding electrolyte
- (C) Change in pH (D) Adding water

Sol.

34. When -vely charged colloid like  $As_2S_3$  sol is added to +vely charged  $Fe(OH)_3$  sol in

suitable amounts

- (A) Both the sols are precipitated simultaneously  
 (B) This process is called mutual coagulation  
 (C) They become +vely charged colloid  
 (D) They become -vely charged colloid

**Sol.**

35. Which of the following is not lyophilic

- (A) Gelatin sol  
 (B) Silver sol  
 (C) Sulphur sol  
 (D)  $As_2S_3$  sol

**Sol.**

36. Colloidal Gold can be prepared by

- (A) Bredig's arc method  
 (B) Reduction of  $AuCl_3$   
 (C) Hydrolysis  
 (D) Peptization

**Sol.**

37. The coagulation of sol particles may be brought about by

- (A) heating  
 (B) adding oppositely charged sol.  
 (C) adding electrolyte  
 (D) persistent dialysis

**Sol.**

38. Which one is not lyophobic in nature ?

- (A) Gelatine (B) Sulphur  
 (C) Starch (D) Protein

**Sol.**

39. Which of the following are colloids ?

- (A) Milk (B) Ice cream  
 (C) Urea solution (D) Blood

**Sol.**

40. Which are the properties of sols ?

- (A) Adsorption  
 (B) Tyndall effect  
 (C) Flocculation  
 (D) Paramagnetism

**Sol.**

41. Which of the following statements are true about AgI sol prepared by peptization of AgI with  $AgNO_3$

- (A) In electrophoresis, the dispersed phase will move towards cathode.  
 (B)  $AlCl_3$  is more effective than  $Na_3PO_4$  for bringing about coagulation of sol.  
 (C) On addition of NaCl in sol, the solution is stabilised  
 (D) On persistent dialysis of sol, precipitation of colloidal sol takes place (coagulation)

**Sol.**

42. **Match the Column**

**Column - I**

- (A) Both Dispersed phase (DP) and Dispersion Medium (DM) are in same physical state  
 (B) DP and DM are in different Physical state  
 (C) DM is liquid  
 (D) DP is liquid

**Column - II**

- (P) Milk  
 (Q) Fog  
 (R) smoke  
 (S) Foam

**Sol.**

43. **Column I**

- A.** Fog  
**B.** Milk  
**C.** Cheese  
**D.** Soap lather

**Column II**

- P.** Gel  
 Foam  
**R.** Emulsion  
**S.** Aerosol

**Sol.**

44. **Column I**

- A.** Electrophoresis  
**B.** Electro-Osmosis  
**C.** Tyndall effect  
**D.** Brownian movement

**Column II**

- P.** Movement of molecules of DM  
**Q.** Mechanical property  
**R.** Optical property  
**S.** Determination of charge on colloidal particle

**Sol.**



**EXERCISE – III****PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

- Q.1** Adding alum to turbid water, impurities are removed due to - **[AIEEE-2002]**  
 (A) Coagulation (B) Brownian movement  
 (C) Electrophoresis (D) Tyndall effect

**Sol.**

- Q.2** Which one of the following characteristics is not correct for physical adsorption ? **[AIEEE-2003]**

- (A) Adsorption is spontaneous  
 (B) Both enthalpy and entropy of adsorption are negative  
 (C) Adsorption on solids is reversible  
 (D) Adsorption increases with increase in temperature

**Sol.**

- Q.3** The volume of a colloidal particle,  $V_c$  as compared to the volume of a solute particle in a true solution  $V_s$ , could be - **[AIEEE-2005]**

- (A)  $\frac{V_c}{V_s} \approx 10^{23}$  (B)  $\frac{V_c}{V_s} \approx 1$   
 (C)  $\frac{V_c}{V_s} \approx 10^3$  (D)  $\frac{V_c}{V_s} \approx 10^{-3}$

**Sol.**

- Q.4** The dispersed phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged, respectively. Which of the following statements is NOT correct ? **[AIEEE-2005]**

- (A) Sodium sulphate solution causes coagulation in both sols  
 (B) Magnesium chloride solution coagulates, the gold sol more readily than the iron (III) hydroxide sol.  
 (C) the processes of electrophoresis provided charge on both the sols  
 (D) Colloidal iron is coagulated by  $Mg^{+2}$  and colloidal gold is coagulated by  $Cl^-$

**Sol.**

- Q.5** In Langmuir's model of adsorption of a gas on a solid surface - **[AIEEE 2006]**

- (A) the adsorption at a single site on the surface may involve multiple molecules at the same time  
 (B) the mass of gas striking a given area of surface is proportional to the pressure of the gas  
 (C) the mass of gas striking a given area of surface is independent of the pressure of the gas  
 (D) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered

**Sol.**

- Q.6** Gold numbers of protective colloids A, B, C and D are 0.50, 0.01, 0.10 and 0.005, respectively. The correct order of their protective powers is **[AIEEE 2008]**  
 (A)  $C < B < D < A$  (B)  $A < C < B < D$   
 (C)  $B < D < A < C$  (D)  $D < A < C < B$

**Sol.**

- Q.7** Which of the following statements is incorrect regarding physisorptions ? **[AIEEE 2009]**  
 (A) More easily liquefiable gases are adsorbed readily  
 (B) Under high pressure it results into multi molecular layer on adsorbent surface  
 (C) Enthalpy of adsorption ( $\Delta H_{\text{adsorption}}$ ) is low and positive  
 (D) If occurs because of van der Waal's forces

**Sol.**

- Q.8** The coagulating power of electrolytes having ions  $Na^+$ ,  $Al^{3+}$  and  $Ba^{2+}$  for arsenic sulphide sol increases in the order:  
 (A)  $Ba^{2+}$ ,  $Na^+$  <  $Al^{3+}$  **[IIT Mains 2013]**  
 (B)  $Al^{3+}$  <  $Na^+$  <  $Ba^{2+}$   
 (C)  $Al^{3+}$  <  $Ba^{2+}$  <  $Na^+$  (D)  $Na^+$  <  $Ba^{2+}$  <  $Al^{3+}$

**Sol.**

## LEVEL – II

## JEE ADVANCED

- Q.1** One gm of charcoal absorbs 100 ml 0.5 M  $\text{CH}_3\text{COOH}$  to form a monolayer, and there by the molarity of  $\text{CH}_3\text{COOH}$  reduces to 0.49. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal =  $3.01 \times 10^2 \text{ m}^2/\text{gm}$

**Sol.** [JEE' 2003]

- Q.2** 20% surface sites have adsorbed  $\text{N}_2$ . On heating  $\text{N}_2$  gas evolved from sites and were collected at 0.001 atm and 298 K in a container or volume is  $2.46 \text{ cm}^3$ . Density of surface sites is  $6.023 \times 10^{14}/\text{cm}^2$  and surface area is  $1000 \text{ cm}^2$ , find out the no. of surface sites occupied per molecule of  $\text{N}_2$ .

**Sol.** [JEE 2005]

- Q.3** **Assertion :** Micelles are formed by surfactant molecules above the critical miceller concentration (CMC).

**Reason :** The conductivity of a solution having surfactant molecules decreases sharply at the CMC.

**Sol.** [JEE 2007]

- Q.4** Among the following the surfactant that will form micelles in aqueous solution at the lowest molar concentration at

- (A)  $\text{CH}_3(\text{CH}_2)_{12}\text{N}^+(\text{CH}_3)_3\text{Br}^-$  [JEE 2008]  
 (B)  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$   
 (C)  $\text{CH}_3(\text{CH}_2)_6\text{COO}^-\text{Na}^+$   
 (D)  $\text{CH}_3(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_3\text{Br}^-$

**Sol.**

- Q.5** Among the electrolytes  $\text{Na}_2\text{SO}_4$ ,  $\text{CaCl}_2$ ,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{NH}_4\text{Cl}$ , the most effective coagulation agent for  $\text{Sb}_2\text{S}_3$  sol is.

[JEE 2009]

- (A)  $\text{Na}_2\text{SO}_4$  (B)  $\text{CaCl}_2$   
 (C)  $\text{Al}_2(\text{SO}_4)_3$  (D)  $\text{NH}_4\text{Cl}$

**Sol.**

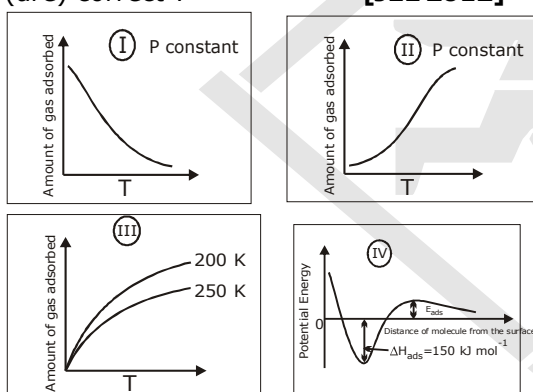
- Q.6** Silver (atomic weight =  $108 \text{ g mol}^{-1}$ ) has a density of  $10.5 \text{ g cm}^{-3}$ . The number of silver atoms on a surface of area  $10^{-12} \text{ m}^2$  can be expressed in scientific notation as  $y \times 10^x$ . The value of x is– [JEE 2010]

**Sol.**

- Q.7** The correct statement(s) pertaining to the adsorption of a gas on a solid surface is (are)  
 (A) Adsorption is always exothermic  
 (B) Physisorption may transform into chemisorption at high temperature.  
 (C) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature.  
 (D) Chemisorption is more exothermic than physisorption, however it is very slow due to higher energy of activation. **[JEE 2011]**

**Sol.**

- Q.8** The given graphs / data I, II, III and IV represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice (s) about I, II, III and IV is (are) correct ? **[JEE 2012]**



- (A) I is physisorption and II is chemisorption  
 (B) I is physisorption and III is chemisorption  
 (C) IV is chemisorption and II is chemisorption  
 (D) IV is chemisorption and III is chemisorption

**Sol.**

- Q.9** Choose the correct reason(s) for the stability of the lyophobic colloidal particles.  
 (A) Preferential adsorption of ions on their surface from the solution **[JEE 2012]**  
 (B) Preferential adsorption of solvent on their surface from the solution  
 (C) Attraction between different particles having opposite charges on their surface  
 (D) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles.

**Sol.**

- 10.** Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process the correct statement is

**[JEE 2013]**

- (A) The adsorption requires activation at 25°C.  
 (B) The adsorption is accompanied by a decrease in enthalpy  
 (C) The adsorption increases with increase of temperature.  
 (D) The adsorption is irreversible.

**ANSWER-KEY****Proficiency Test**

- 1.**
- |                               |                      |                     |
|-------------------------------|----------------------|---------------------|
| 1. Adsorbent                  | 2. Desorption        | 3. Electrophoresis  |
| 4. 20–40 kJ·mol <sup>-1</sup> | 5. Brownian movement | 6. More             |
| 7. Electrophoresis            | 8. Scattering        | 9. Emulsions        |
|                               |                      | 10. Electro-osmosis |
| 11. Solid in gas              | 12. Adsorption       | 13. Gold number     |
|                               |                      | 14. Emulsion        |
|                               |                      | 15. Gel             |
- 2.**
- |      |      |      |      |       |
|------|------|------|------|-------|
| 1. T | 2. T | 3. F | 4. F | 5. T  |
| 6. T | 7. F | 8. F | 9. T | 10. T |

**Answer Ex-I****OBJECTIVE PROBLEMS (JEE MAIN)**

Select the correct alternative. (Only one is correct)

- |       |       |       |       |       |
|-------|-------|-------|-------|-------|
| 1. B  | 2. D  | 3. C  | 4. B  | 5. D  |
| 6. A  | 7. B  | 8. B  | 9. D  | 10. B |
| 11. C | 12. B | 13. B | 14. D | 15. A |
| 16. D | 17. B | 18. C | 19. A | 20. A |
| 21. B | 22. A | 23. B | 24. C | 25. B |
| 26. C | 27. C | 28. C | 29. D | 30. B |
| 31. B | 32. B | 33. D | 34. A | 35. C |

**Answer Ex-II****OBJECTIVE PROBLEMS (JEE ADVANCED)**

- |       |       |       |         |       |
|-------|-------|-------|---------|-------|
| 1. D  | 2. D  | 3. B  | 4. B    | 5. B  |
| 6. A  | 7. C  | 8. B  | 9. A    | 10. A |
| 11. A | 12. B | 13. D | 14. C   | 15. A |
| 16. B | 17. A | 18. D | 19. B,D | 20. A |
| 21. B | 22. C | 23. C | 24. C   | 25. B |
| 26. B | 27. C |       |         |       |

Select the correct alternative. (More than one are correct)

28. A,B,D      29. A,B,D      30. A,B      31. A,B      32. A,B,D  
 33. A,B,C      34. A,B      35. B,C,D      36. A,B      37. A,B,C,D  
 38. A,C,D      39. A,B,D      40. A,B,C      41. A,D  
 42. A-P; B-Q,R,S, ; C-P,S ; D-P,Q      43. A - S ; B - R ; C - P ; D - Q  
 44. A - S ; B - P ; C - R ; D - Q

### Answer Ex-III

### PREVIOUS YEARS PROBLEMS

#### LEVEL – I

#### JEE MAIN

1. A      2. D      3. C      4. D      5. B  
 6. B      7. C      8. D

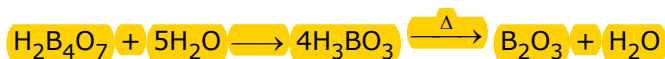
#### LEVEL – II

#### JEE ADVANCED

1.  $5 \times 10^{-19} \text{ m}^2$       2. 0.0002      3. B      4. A      5. C  
 6. 0.007      7. ABD      8. AC      9. AD      10. B

**p-Block Elements****Group-III****Isolation of "B" :**

- (i) Preparation of
- $B_2O_3$
- from Borax or Colemanite



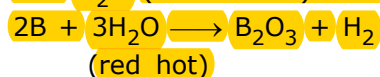
- (ii) Reduction of
- $B_2O_3$

**Chemical Props. :**

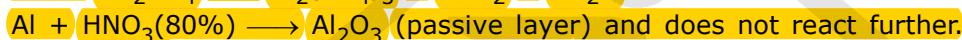
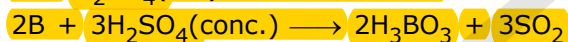
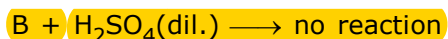
- (i) Burning in air :



- (ii) Reaction with water



- (iii)
- $B + HCl \longrightarrow$
- no reaction



- (iv)
- $2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$



- (v)
- $2B + N_2 \longrightarrow 2BN$
- $2Al + N_2 \longrightarrow 2AlN$



- (vi)
- $3Mg + 2B \longrightarrow Mg_3B_2$

**Preparation of  $B_2H_6$  :**

- (i)
- $Mg_3B_2 + HCl (10\%) \longrightarrow B_2H_6 + B_4H_{10} + B_5H_9$
- etc.

- (ii)
- $B_4H_{10} \xrightarrow[100^\circ C]{\Delta} B_2H_6 + H_2 + \text{higher borane}$

- (iii)
- $BCl_3$
- (or
- $BBr_3$
- ) +
- $6H_2 \xrightarrow[\text{at low temperature}]{\text{Electric discharge}} B_2H_6 + 6HCl$

- (iv)
- $3LiAlH_4$
- or
- $(LiBH_4) + 4BF_3 \longrightarrow 3LiF + 3AlF_3$
- or
- $3(BF_3) + 2B_2H_6$

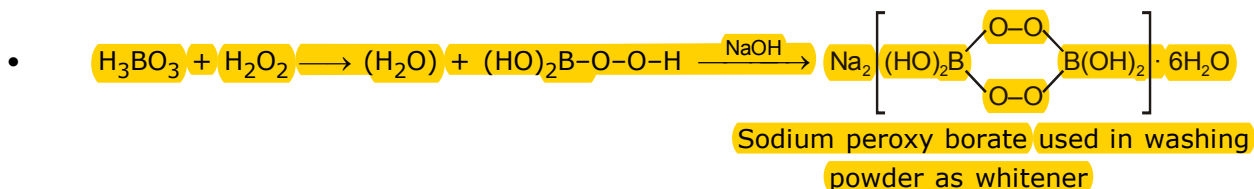
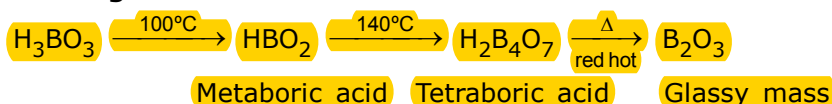
**Reaction of  $B_2H_6$  :**

- (i)
- $B_2H_6 + O_2 \xrightarrow[\text{spontaneously}]{\text{burns in air}} B_2O_3 + H_2O$

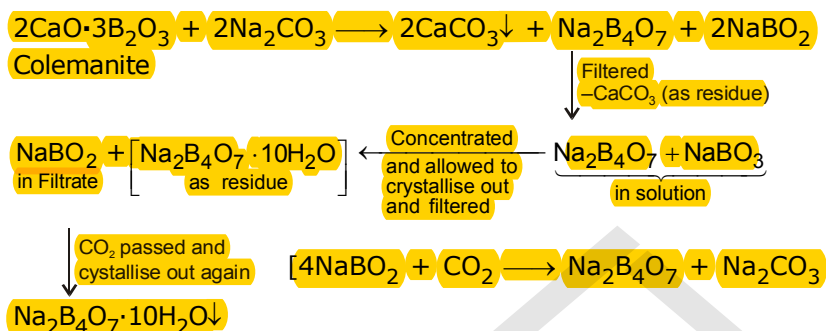
- (ii)
- $B_2H_6 + H_2O$
- (Cold is enough)
- $\longrightarrow H_3BO_3 + 6H_2$

- (iii)
- $B_2H_6 + HCl$
- (dyl)
- $\xrightarrow[AlCl_3]{\text{anh.}} B_2H_5Cl + H_2$

• **Heating of Boric Acid :**



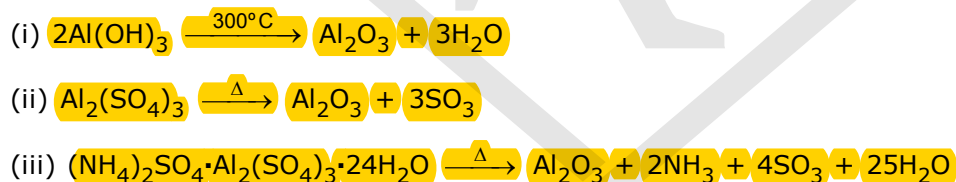
**Preparation of Borax :**



**Uses of Borax :**

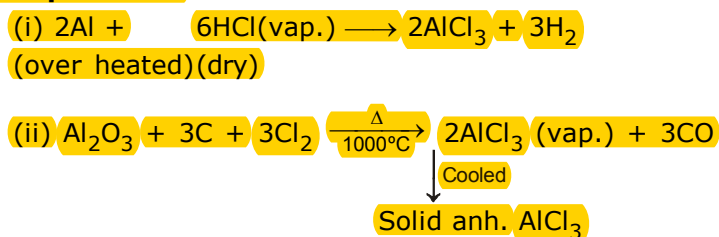
- (i) In making glass, enamel and gaze or pottery.
- (ii) As antiseptics in medicinal soaps preparation.

**Al<sub>2</sub>O<sub>3</sub> preparation :**



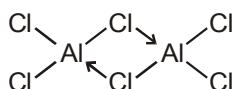
- Uses :** (i) In making refractory brick
- (ii) as abrasive
- (iii) To make high alumina cement

**AlCl<sub>3</sub> Preparation :**



**Props :**

- (i) Its anhydrous form is deliquescent and fumes in air.
- (ii) It sublimes at  $180^{\circ}\text{C}$ .
- (iii) It is covalent and exists in the form of dimer even if in non polar solvents e.g. alc., ether, benzene, where it is soluble in fair extent.

**Uses :** (i) Friedel-Craft reaction

- (ii) Dyeing, drug & perfumes etc.

**Alumns :**  $\text{M}_2\text{SO}_4, \text{M}'_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  **Props :** Swelling characteristics

where  $\text{M} = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{As}^+, \text{Ti}^+, \text{NH}_4^+$

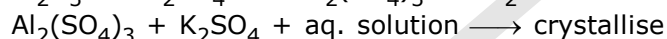
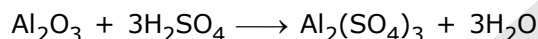
$\text{M}' = \text{Al}^{+3}, \text{Cr}^{+3}, \text{Fe}^{+3}, \text{Mn}^{+3}, \text{Co}^{+3}$

$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  Potash alum

$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  Ammonium alum

$\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  Chrome alum

$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  Ferric alum

**Preparation :**

- Uses :** (i) Act as coagulant. (ii) Purification of water (iii) Tanning of leather  
(iv) Mordant in dyeing (v) Antiseptic

**Group-IV****Types of Carbide :**

- (i) Ionic and salt like classification on basis of no. of carbon atoms present in hydrocarbon found on their hydrolysis

- (a)  $\text{C}_1$  unit
- (b)  $\text{C}_2$  unit
- (c)  $\text{C}_3$  unit

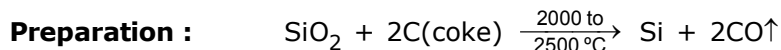
**$\text{C}_1$  unit :**  $\text{Al}_4\text{C}_3, \text{Be}_2\text{C}$   
 $\text{Be}_2\text{C} + \text{H}_2\text{O} \longrightarrow \text{Be}(\text{OH})_2 + \text{CH}_4$   
 $\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \longrightarrow 4\text{Al}(\text{OH})_3 + 3\text{CH}_4$

**$\text{C}_2$  unit :**  $\text{CaC}_2, \text{BaC}_2$   
 $\text{CaC}_2 + 12\text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_2 + \text{CH} \equiv \text{CH}$

**$\text{C}_3$  unit :**  $\text{Mg}_2\text{C}_3$   
 $\text{Mg}_2\text{C}_3 + \text{H}_2\text{O} \longrightarrow 2\text{Mg}(\text{OH})_2 + \text{CH}_3\text{-C} \equiv \text{CH} : \text{Propyne}$

- (ii) Covalent carbide :  $\text{SiC}$  &  $\text{B}_4\text{C}$
- (iii) Interstitial carbide :  $\text{MC}$  (Transition element or inner transitional elements forms this kind of carbide) Interstitial carbide formation doesn't affect the metallic lustre and electrical conductivity. ( $\therefore$  no chemical bond is present, no change in property.)



SiC

when impurity is present

**Properties :**

- (i) It is very hard and is used in cutting tools and abrasive powder (polishing material).
- (ii) It is very much inert.
- (iii) It is not being affected by any acid except  $\text{H}_3\text{PO}_4$ .

CO

- How to detect
- How to estimate
- What are its absorbers

(i) How to detect

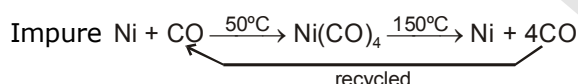
- (a) burns with blue flame.
- (b) CO is passed through  $\text{PdCl}_2$  solution giving rise to black ppt.



Black metallic deposition

(ii) How to estimate(iii) What are its absorbers**Uses :**

In the Mond's process of Ni-extraction  
CO is the purifying agent for Ni

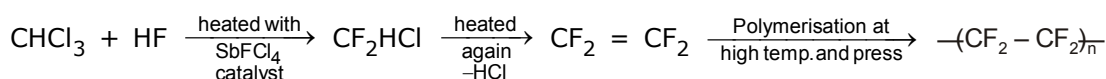


Producer gas :  $\text{CO} + \text{N}_2 + \text{H}_2$

Water gas :  $\text{CO} + \text{H}_2$

Water gas is higher calorific value than producer gas.

$\therefore$  in water gas, both CO &  $\text{H}_2$  burns while in producer gas  $\text{N}_2$  doesn't burn.

**Taflon**  $-(\text{CF}_2 - \text{CF}_2)_n-$ **Purpose**

Temp. withstanding capacity upto  $500-550^\circ\text{C}$  (1<sup>st</sup> organic compound withstand this kind of high temperature.)

**SILICON (Si)****Occurrence :**

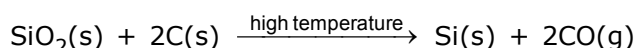
Silicon is the second most abundant (27.2%) element after oxygen (45.5%) in the earth's crust. It does not occur free in nature but in the combined state, it occurs widely in form of silica and silicates. All mineral rocks, clays and soils are built of silicates of magnesium, aluminium, potassium or iron. Aluminium silicate is however the most common constituent of rocks and clays.

Silica is found in the free state in sand, flint and quartz and in the combined state as silicates like

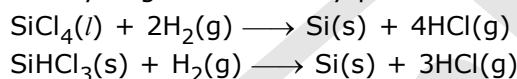
- (i) Feldspar –  $K_2O \cdot Al_2O_3 \cdot 6SiO_2$
- (ii) Kaolinite –  $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
- (iii) Asbestos –  $CaO \cdot 3MgO \cdot 4SiO_2$

**Preparation :**

- (i) From silica (sand) : Elemental silicon is obtained by the reduction of silica ( $SiO_2$ ) with high purity coke in an electric furnace.



- (ii) From silicon tetrachloride ( $SiCl_4$ ) or silicon chloroform ( $SiHCl_3$ ) : Silicon of very high purity required for making semiconductors is obtained by reduction of highly purified silicon tetrachloride or silicon chloroform with dihydrogen followed by purification by zone refining.

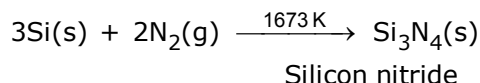
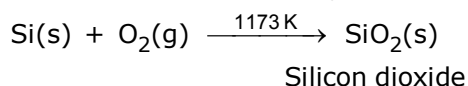
**Physical Properties :**

- (i) Elemental silicon is very hard having diamond like structure.
- (ii) It has shining luster with a melting point of 1793 K and boiling point of about 3550 K.
- (iii) Silicon exists in three isotopes, i.e.  ${}^{28}_{14}Si$ ,  ${}^{29}_{14}Si$  and  ${}^{30}_{14}Si$  but  ${}^{28}_{14}Si$  is the most common isotope.

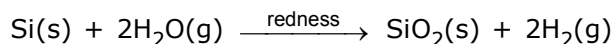
**Chemical Properties :**

Silicon is particularly unreactive at room temperature towards most of the elements except fluorine. Some important chemical reactions of silicon are discussed below.

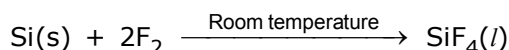
- (i) **Action of air :** Silicon reacts with oxygen of air at 1173 K to form silicon dioxide and with nitrogen of air at 1673 K to form silicon nitride,



- (ii) **Action of steam :** It is slowly attacked by steam when heated to redness liberating dihydrogen gas.

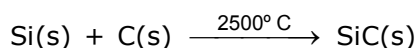


- (iii) **Reaction with halogens :** It burns spontaneously in fluorine gas at room temperature to form silicon tetrafluoride ( $SiF_4$ ).



However, with other halogens, it combines at high temperature forming tetrahalides.

- (iv) **Reaction with carbon :** Silicon combines with carbon at 2500°C forming silicon carbide (SiC) known as carborundum.



Carborundum is an extremely hard substance next only to diamond. It is mainly used as an abrasive and as a refractory material.

#### Uses :

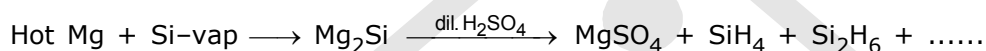
- Silicon is added to steel as such or more usually in form of ferrosilicon (an alloy of Fe and Si) to make it acid-resistant.
- High purity silicon is used as semiconductors in electronic devices such as transistors.
- It is used in the preparation of alloys such as silicon-bronze, magnesium silicon bronze and ferrosilicon.

#### Compounds of Silicon :

What is silane.  $\text{Si}_n\text{H}_{2n+2}$   $\text{SiH}_4$  &  $\text{Si}_2\text{H}_6$

Only these two are found

Higher molecules are not formed.  $\therefore$  Si can't show catenation property.



**Ques.**  $\text{SiH}_4$  is more reactive than  $\text{CH}_4$ . Explain.

#### Reasons :

- (i)  $\text{Si}^{\delta+} - \text{H}^{\delta-}$  in  $\text{C}^{\delta-} - \text{H}^{\delta+}$

C - electro -ve than H

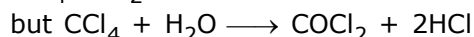
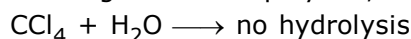
Si less electro -ve than H

So bond polarity is reversed when  $\text{Nu}^-$  attacks, it faces repulsion in C but not in Si.

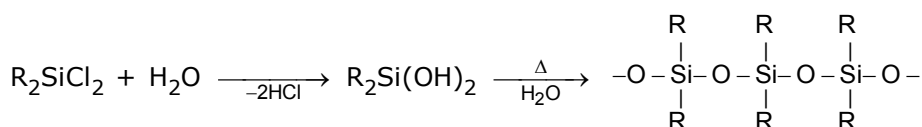
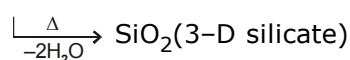
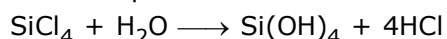
- Silicon is having vacant d orbital which is not in case of carbon.
- Silicon is larger in size compared to C. By which the incoming  $\text{Nu}^-$  doesn't face any steric hindrance to attack at Si whereas  $\text{CH}_4$  is tightly held from all sides.

#### Silicones :

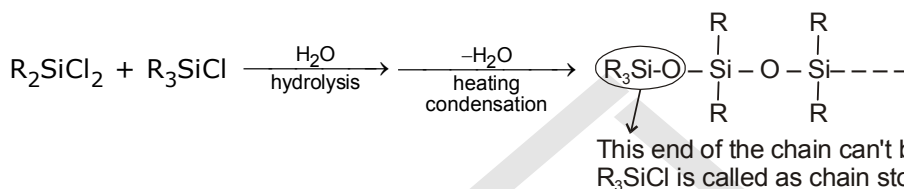
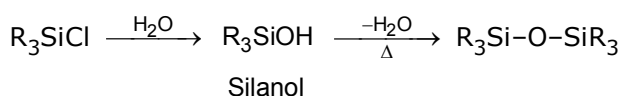
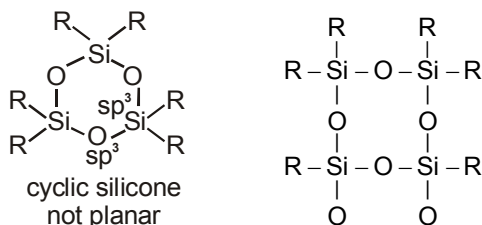
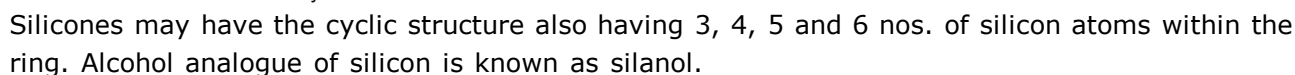
It is organo silicon polymer,



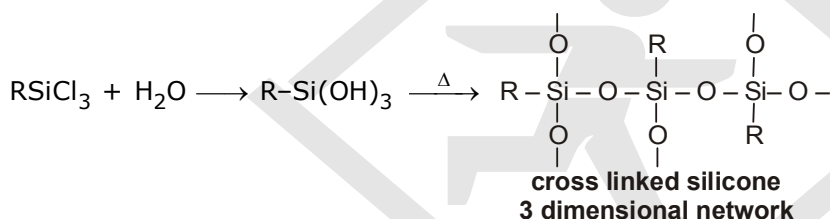
super heated steam



**Linear silicone**



\* Using  $R_3SiCl$  in a certain proportion we can control the chain length of the polymer.



It provides the crosslinking among the chain making the polymer more hard and hence controlling the proportion of  $\text{RSiCl}_3$  we can control the hardness of polymer.

### Uses :

- (1) It can be used as electrical insulator (due to inertness of Si-O-Si bonds).
- (2) It is used as water repellent ( $\because$  surface is covered) eg. car polish, shoe polish, masonry work in buildings.
- (3) It is used as antifoaming agent in sewage disposal, beer making and in cooking oil used to prepare potato chips.
- (4) As a lubricant in the gear boxes.

### Silica (SiO<sub>2</sub>)

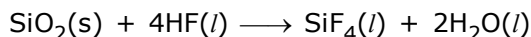
**Occurrence :**

Silica or silicon dioxide occurs in nature in the free state as sand, quartz and flint and in the combined state as silicates like, Feldspar :  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ , Kaolinite :  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  etc.

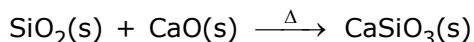
**Properties :**

- (i) Pure silica is colourless, but sand is usually coloured yellow or brown due to the presence of ferric oxide as an impurity.

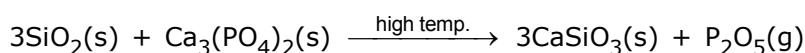
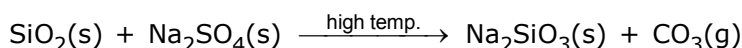
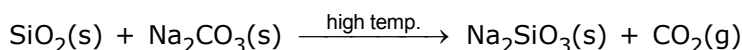
- (ii) Silicon dioxide is insoluble in water and all acids except hydrofluoric acid.



- (iii) It also combines with metallic oxides at high temperature giving silicates e.g.,



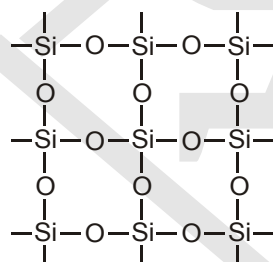
- (iv) When silica is heated strongly with metallic salts, silicates are formed and the volatile oxides are driven off as vapours.



The first two examples quoted here are important in glass making.

**Structure of Silica :**

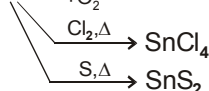
Silica has a three-dimensional network structure. In silica, silicon is  $\text{sp}^3$ -hybridized and is thus linked to four oxygen atoms and each oxygen atom is linked to two silicon atoms forming a three-dimensional giant molecule as shown in figure. This three-dimensional network structure imparts stability to  $\text{SiO}_2$  crystal and hence a large amount of energy is required to break the crystal resulting in high melting point.

**Uses :**

- (i) Sand is used in large quantities to make mortar and cement.
- (ii) Being transparent to ultraviolet light, large crystal of quartz are used for making lenses for optical instruments and for controlling the frequency of radio-transmitters.
- (iii) Powdered quartz is used for making silica bricks.
- (iv) Silica gel ( $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ ) is used as a desiccant (for absorbing moisture) and as an absorbent in chromatography.

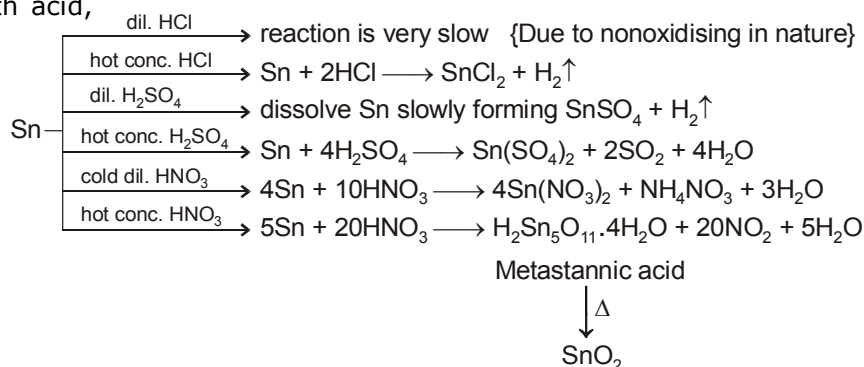
**Tin & Its Compound**

- (i)  $\text{Sn} \xrightarrow[+\text{O}_2]{1500^\circ\text{C}} \text{SnO}_2$  [Burns with a bright flame]

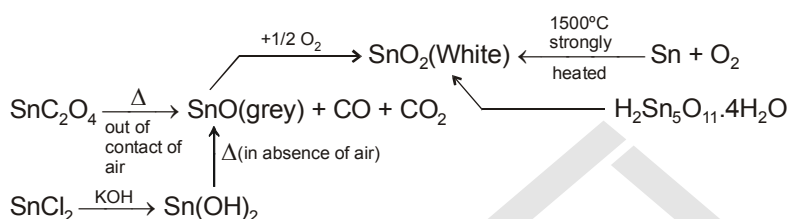
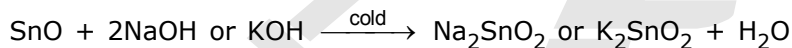
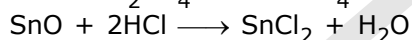
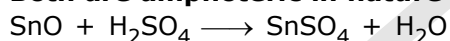


- (ii)  $\text{Sn} + 2\text{H}_2\text{O} \xrightarrow{\text{Room temp.}} \text{No reaction}$   
 $\text{Sn} + 2\text{H}_2\text{O} \xrightarrow{\text{At high temp.}} \text{SnO}_2 + 2\text{H}_2$

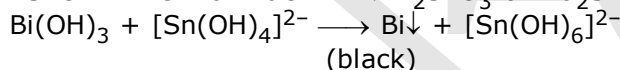
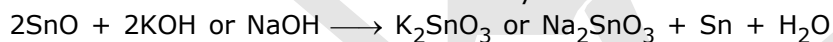
(iii) Reaction with acid,

(iv)  $\text{Sn} + 2\text{NaOH} + \text{H}_2\text{O} \longrightarrow \text{Na}_2\text{SnO}_3 + 2\text{H}_2\uparrow$ .

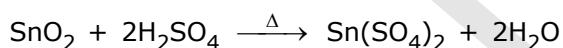
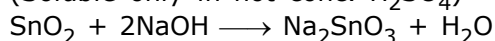
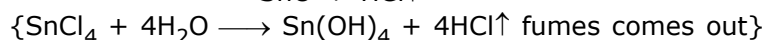
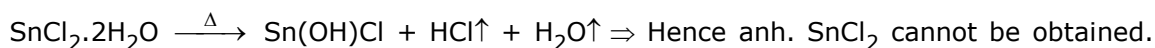
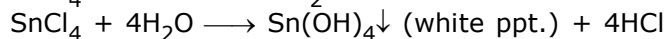
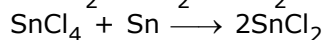
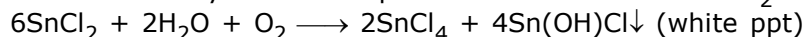
or

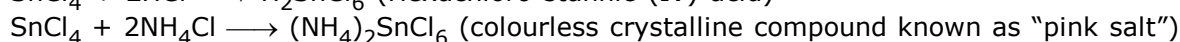
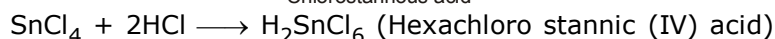
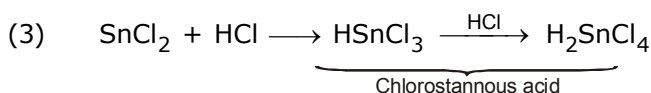
KOH [In absence of air  $\text{Na}_2\text{SnO}_2$  forms and in contact with air it readily converts into  $\text{Na}_2\text{SnO}_3$ .]**Oxides :  $\text{SnO}$ (grey) &  $\text{SnO}_2$ (white)****Both are amphoteric in nature :**

But conc. hot alkali behaves differently.

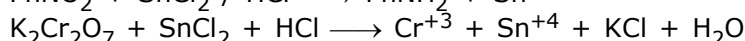
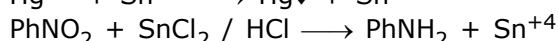


(black)

(Soluble only in hot conc.  $\text{H}_2\text{SO}_4$ ) **$\text{SnCl}_2$  &  $\text{SnCl}_4$  :**(1)  $\text{Sn} + 2\text{HCl} \text{ (hot conc.)} \longrightarrow \text{SnCl}_2 + \text{H}_2\uparrow$ (2) A piece of Sn is always added to preserved a solution of  $\text{SnCl}_2$ . Explain.

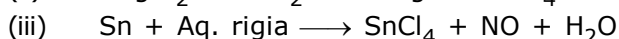
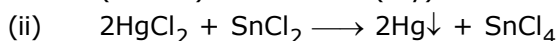
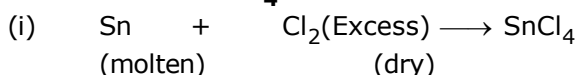


(4) Red Prop. of  $\text{SnCl}_2$  :



(5) Readily combines with  $\text{I}_2 \Rightarrow \text{SnCl}_2\text{I}_2 \Rightarrow$  This reaction is used to estimate tin.

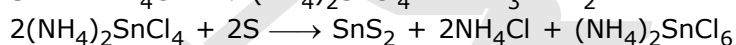
#### Formation of $\text{SnCl}_4$ :



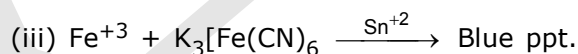
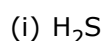
\*  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  is known as butter of tin  $\Rightarrow$  used as mordant.

$(\text{NH}_4)_2\text{SnCl}_6$  is known as 'pink salt'  $\Rightarrow$  used as calico printing.

**Mosaic gold :**  $\text{SnS}_2$  yellow crystalline substance :

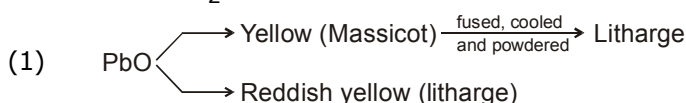
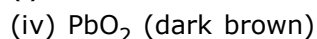
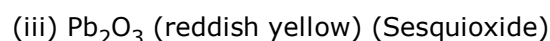
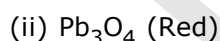


\* **Distinction of  $\text{Sn}^{+2}$  /  $\text{Sn}^{+4}$  :**

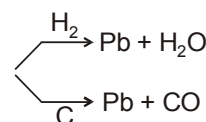
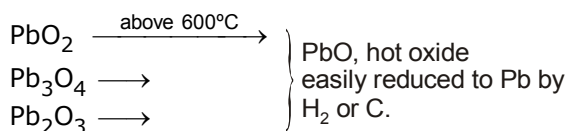
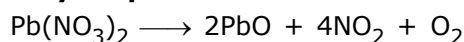


#### Compound of Lead

**Oxides of Lead :**



#### Laboratory Preparation :



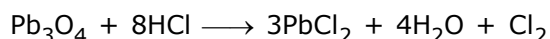
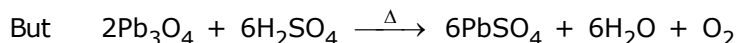
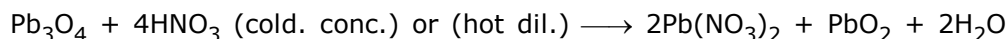
#### Preparation of $\text{Pb}_2\text{O}_3$ :



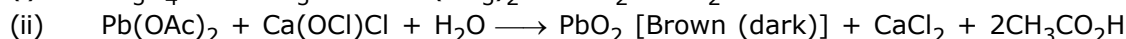
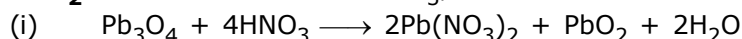
hot solution of it in NaOH      Limited amount

$\text{Pb}_2\text{O}_3 + 2\text{HNO}_3 \longrightarrow \text{PbO}_2\downarrow + \text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{O}$   
This reaction suggest that  $\text{Pb}_2\text{O}_3$  contains  $\text{PbO}_2$ .

(2)  **$\text{Pb}_3\text{O}_4$**  :  $6\text{PbO} + \text{O}_2 \xrightleftharpoons[>470^\circ\text{C}]{340^\circ\text{C}} 2\text{Pb}_3\text{O}_4$  (In the same way, prove that its formula is  $2\text{PbO}.\text{PbO}_2$ )

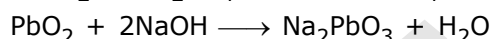
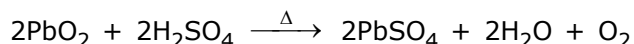


(3)  **$\text{PbO}_2$**  : Insoluble in water.  $\text{HNO}_3$ , But reacts with  $\text{HCl} + \text{H}_2\text{SO}_4$  (hot conc.) and in hot  $\text{NaOH}/\text{KOH}$ .

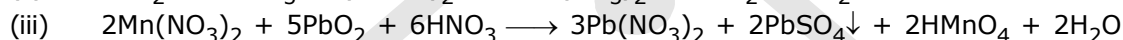
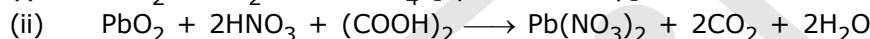
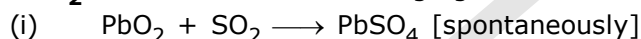


↓

Excess bleaching powder is being removed by stirring with  $\text{HNO}_3$ .



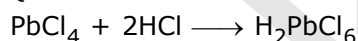
**$\text{PbO}_2$**  : Powerful oxidising agent :



**$\text{PbCl}_4$**  : Exists as  $\text{H}_2[\text{PbCl}_6]$



{ice cold conc. saturated with  $\text{Cl}_2$ }



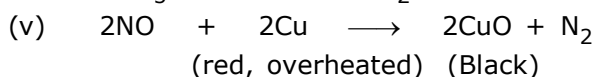
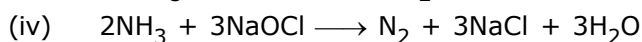
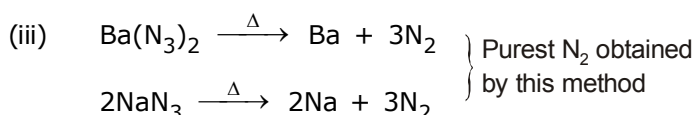
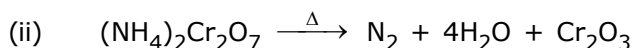
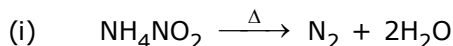
**TetraEthyl lead :**



It is antiknocking agent.

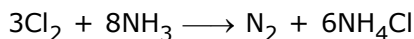
### Group – V

**Preparation of  $\text{N}_2$  :**

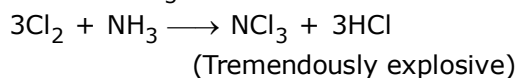




- (vi)  $\text{Cl}_2$  passed into liquor  $\text{NH}_3$   
 $3\text{Cl}_2 + 2\text{NH}_3 \longrightarrow \text{N}_2 + 6\text{HCl}$   
 $6\text{NH}_3 + 6\text{HCl} \longrightarrow 6\text{NH}_4\text{Cl}$

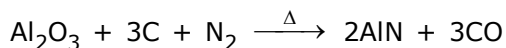
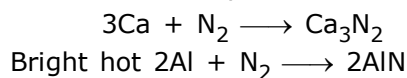


In this method  $\text{NH}_3$  conc. should not be lowered down beyond a particular limit.

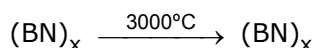


### Properties of $\text{N}_2$ :

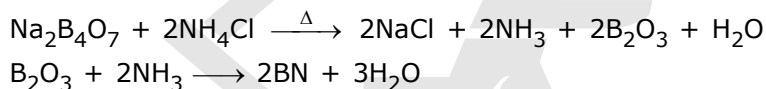
- (i) It is inert due to high bond energy.  
 (ii) It is absorbed by hot metal like Ca, Mg, Al etc.



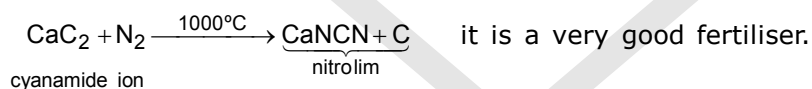
**(BN)<sub>x</sub> :** Inorganic graphite  
 White slippery solid having 2D-sheet structure.



3-D network structure similar to diamond (Borazon) which is harder than diamond and used for diamond cutting.



- (iii)  $\text{N}_2$  can be absorbed by calcium carbide at the temp around  $1000^\circ\text{C}$ ,  $\text{CaC}_2$



- (iv)  $(\text{Ca}(\text{NCN}) + \text{C}) + 3\text{H}_2\text{O} \longrightarrow \text{CaCO}_3 + 2\text{NH}_3 + \text{C}$
- $\swarrow$  Slowly decomposes  $\nearrow$   
 $\text{NH}_2\text{--CO--NH}_2$   
 (Intermediate formed)

### TYPES OF NITRIDE :

- (i) Salt like or ionic :  $\text{Li}_3\text{N}$ ,  $\text{Na}_3\text{N}$ ,  $\text{K}_3\text{N}$  (?),  $\text{Ca}_3\text{N}_2$ ,  $\text{Mg}_3\text{N}_2$ ,  $\text{Be}_3\text{N}_2$   
 (ii) Covalent :  $\text{AlN}$ ,  $\text{BN}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{Ge}_3\text{N}_4$ ,  $\text{Sn}_3\text{N}_4$

- (iii) Interstitial : MN ( $M = \text{Sc, Ti, Zr, Hf, La}$ )  
HCP or FCC

No of metal atom per unit cell is equal to no of octahedral voids per unit cell.

All the octahedral voids are occupied by nitrogen atoms. Hence the formula is MN.

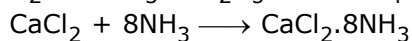
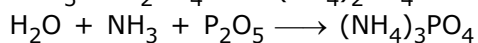
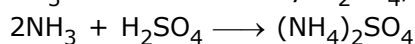
**HCP** : Hexagonal closed pack

**FCC** : Face centred cubic

### NH<sub>3</sub> preparation :

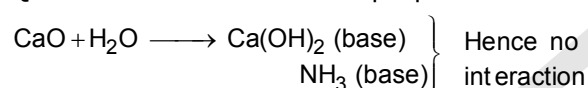
- (i) Nitrate or nitrite reduction :  $\text{NO}_3^- / \text{NO}_2^- + \text{Zn or Al} + \text{NaOH} \longrightarrow \text{NH}_3 + [\text{Zn}(\text{OH})_4]^{2-} \text{ or } [\text{Al}(\text{OH})_4]^-$
- (ii) Metal nitride hydrolysis :  $\text{N}^{3-} + 3\text{H}_2\text{O} \longrightarrow \text{NH}_3 \uparrow + 3\text{OH}^-$
- (iii) Haber's process :  $\text{N}_2 + 3\text{H}_2 \xrightarrow[200-1000 \text{ atm catalyst Fe/Mo}]{450^\circ\text{C}} 2\text{NH}_3$

**Q.1** NH<sub>3</sub> can't be dried by H<sub>2</sub>SO<sub>4</sub>, P<sub>2</sub>O<sub>5</sub> and anh. CaCl<sub>2</sub> because :



forms adduct

Quick lime is used for this purpose



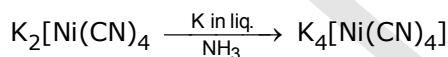
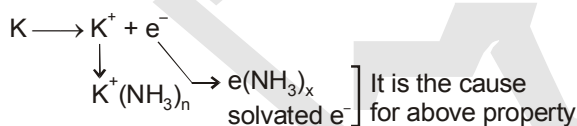
### Properties :

- (i) It dissolves several electropositive metals like Li, Na, K, Rb, Cs, Sr, Ba etc.

Eg. : K in liq NH<sub>3</sub>  $\Rightarrow$  (i) Blue in colour

(ii) Conducts electricity

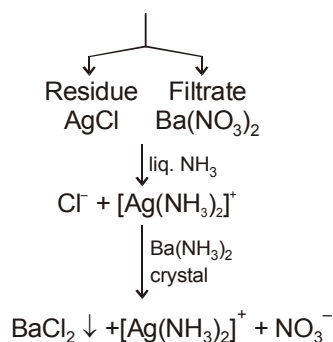
(iii) having reducing property



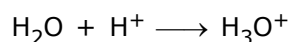
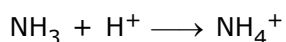
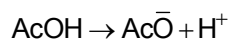
Square planar  
complex

Tetrahedral  
complex

- (ii)  $\text{Ag}(\text{NO}_3)(\text{aq}) + \text{BaCl}_2(\text{aq}) \longrightarrow \text{AgCl} \downarrow + \text{Ba}(\text{NO}_3)_2$



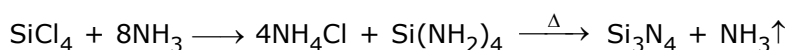
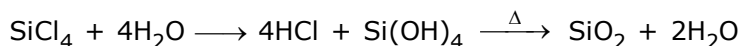
(iii)  $\text{CH}_3\text{COOH}$  is strong acid in liq.  $\text{NH}_3$  while in water is weak acid.



Basidity order  $\text{NH}_3 > \text{H}_2\text{O}$

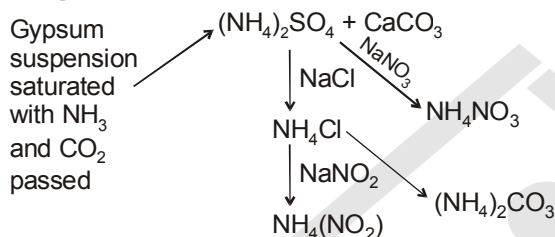
more solvation of  $\text{H}^+$  in  $\text{NH}_3$ .

(iv) Hydrolysis and Ammonolysis occurs in a same way.



Rate of hydrolysis and Ammonolysis will be affected by the presence of  $\text{HCl}$  vapour &  $\text{NH}_4\text{Cl}$  vapour respectively.

### $\text{NH}_4^+$ – Salts Preparation

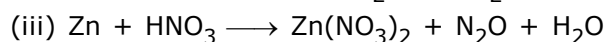
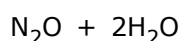
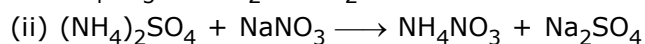
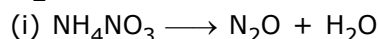


### Oxides of Nitrogen :

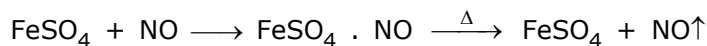
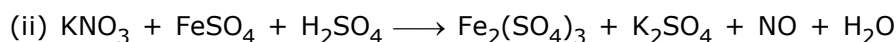
Oxides of Nitrogen	Structure	Physical state	colour of gas
$\text{N}_2\text{O}$	$\bar{\text{N}} = \overset{+}{\text{N}} = \text{O}$	Gas	Colourless
$\text{NO}$	$:\ddot{\text{N}} = \ddot{\text{O}}:$ or $:\text{N} \equiv \text{O}:$	Gas	Colourless
$\text{N}_2\text{O}_3$	$\text{O}=\text{N}-\text{N}=\text{O}$ ; $\text{O}=\text{N}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{N}}}$	Gas	Blue liquid ( $-30^\circ\text{C}$ )
$\text{NO}_2$	$2\text{N} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \rightleftharpoons \text{O}=\text{N}-\text{N}=\text{O}$	Gas	Brown
$\text{N}_2\text{O}_5$	$\text{O}=\text{N}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{N}}}=\text{O}$	Colourless solid	-(no existence in gas phase)

### Preparations :

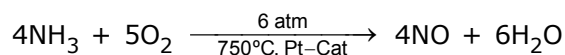
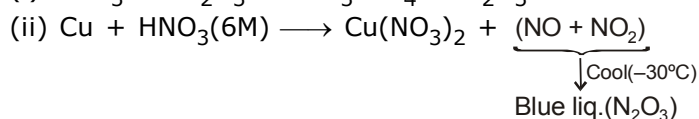
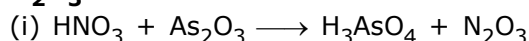
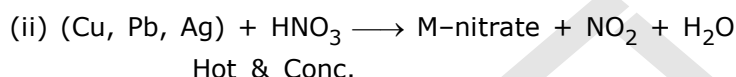
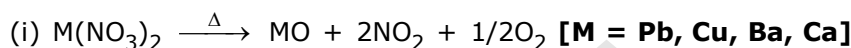
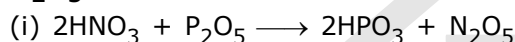
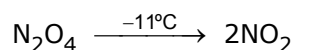
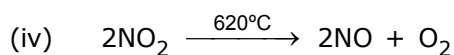
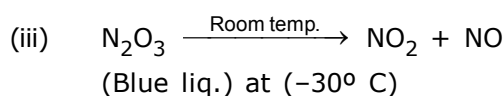
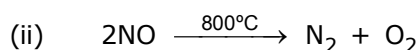
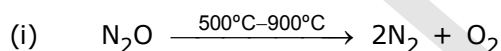
#### 1. $\text{N}_2\text{O}$ :



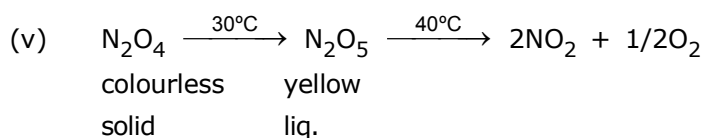
(dil.&Cold)

2. **NO :**

(iii) Ostwald process – Restricted oxidation of  $\text{NH}_3$ .

**Industrial process :**3.  **$\text{N}_2\text{O}_3$  :**4.  **$\text{NO}_2$  :**5.  **$\text{N}_2\text{O}_5$  :****Properties :****(I) Decomposition Behaviour :**

(white solid) Brown gas  
at  $(-11^\circ\text{C})$

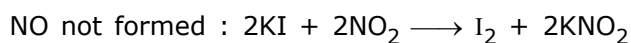
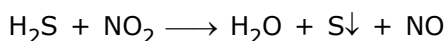
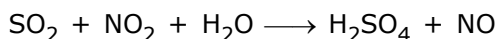


**(II) Reaction with H<sub>2</sub>O & NaOH :**

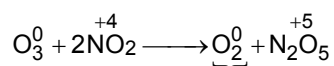
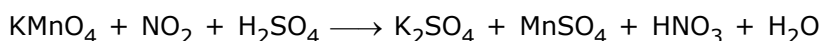
	<b>H<sub>2</sub>O</b>	<b>NaOH</b>
(i)	N <sub>2</sub> O : Fairly soluble in water and produces neutral solution	.....
(ii)	NO : Sparingly soluble in water and produces neutral solution	.....
(iii)	N <sub>2</sub> O <sub>3</sub> : 2HNO <sub>2</sub> Hence it is known as anhydride of HNO <sub>2</sub>	NaNO <sub>2</sub>
(iv)	NO <sub>2</sub> : HNO <sub>2</sub> + HNO <sub>3</sub> called as mixed anhydride	NaNO <sub>2</sub> + NaNO <sub>3</sub>
(v)	N <sub>2</sub> O <sub>5</sub> : 2HNO <sub>3</sub> called as anhydride of HNO <sub>3</sub>	NaNO <sub>3</sub>

**Other properties :**

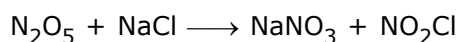
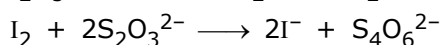
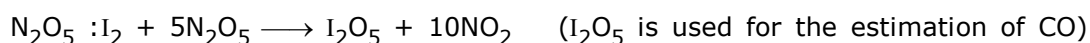
- N<sub>2</sub>O :  $2\text{N}_2\text{O} \longrightarrow 2\text{N}_2 + \text{O}_2$   
 Hence it is better supporter for combustion {mixture contains 33% O<sub>2</sub> compared to 20% in air}
- S + N<sub>2</sub>O  $\longrightarrow$  SO<sub>2</sub> + N<sub>2</sub>  
 P + N<sub>2</sub>O  $\longrightarrow$  P<sub>2</sub>O<sub>5</sub> + N<sub>2</sub>  
 Mg + N<sub>2</sub>O  $\longrightarrow$  MgO + N<sub>2</sub>  
 Na + N<sub>2</sub>O  $\longrightarrow$  Na<sub>2</sub>O + N<sub>2</sub>  
 Cu + N<sub>2</sub>O  $\longrightarrow$  CuO + N<sub>2</sub>  
 H<sub>2</sub> + N<sub>2</sub>O  $\longrightarrow$  H<sub>2</sub>O + N<sub>2</sub>
- NO :
- (i) It burns :  $\text{NO} + 1/2 \text{O}_2 \longrightarrow \text{NO}_2$
  - (ii) It supports combustion also for molten sulphur and hot phosphorous.  
 $\text{S} + 2\text{NO} \longrightarrow \text{SO}_2 + \text{N}_2$   
 $2\text{P} + 5\text{NO} \longrightarrow \text{P}_2\text{O}_5 + 5/2 \text{N}_2$
  - (iii) It is being absorbed by FeSO<sub>4</sub> solution.
  - (iv) It is having reducing property.  
 $\text{KMnO}_4 + \text{NO} + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{HNO}_3 + \text{H}_2\text{O}$   
 $\text{HOCl} + \text{NO} + \text{H}_2\text{O} \longrightarrow \text{HNO}_3 + \text{HCl}$
  - (v) NO shows oxidising property also.  
 $\text{SO}_2 + 2\text{NO} + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + \text{N}_2\text{O}$   
 $\text{H}_2\text{S} + 2\text{NO} \longrightarrow \text{H}_2\text{O} + \text{S} \downarrow + \text{N}_2\text{O}$   
 $3\text{SnCl}_2 + 2\text{NO} + 6\text{HCl} \longrightarrow 3\text{SnCl}_4 + 2\text{NH}_2\text{OH}$   
 (Used for NH<sub>2</sub>OH) preparation)
  - (vi) NO combines with X<sub>2</sub> (X<sub>2</sub> = Cl<sub>2</sub>Br<sub>2</sub>F<sub>2</sub>) to produce NO X.  
 $2\text{NO} + \text{X}_2 \longrightarrow 2\text{NOX}$
- N<sub>2</sub>O<sub>3</sub> : No more properties.
- NO<sub>2</sub> :
- (1) It is having oxidising property.  
 $\text{S} + \text{NO}_2 \longrightarrow \text{SO}_2 + \text{NO}$   
 $\text{P} + \text{NO}_2 \longrightarrow \text{P}_2\text{O}_5 + \text{NO}$   
 $\text{C} + \text{NO}_2 \longrightarrow \text{CO}_2 + \text{NO}$



(2) Reducing property of  $\text{NO}_2$ .



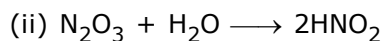
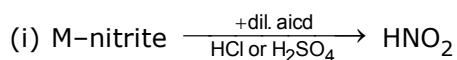
not the reduction product of  $\text{O}_3$



It proves that  $\text{N}_2\text{O}_5$  is consisting of ion pair of  $\text{NO}_2^+$  &  $\text{NO}_3^-$ .

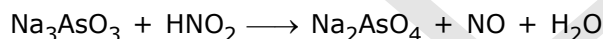
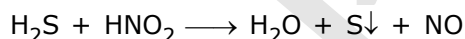
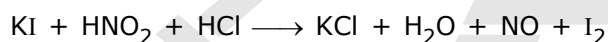
### Oxyacids of N :

#### $\text{HNO}_2$ : Preparation

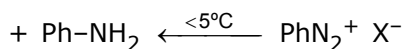
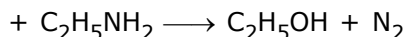
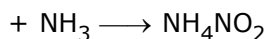
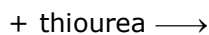
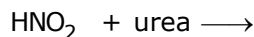
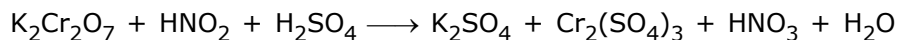
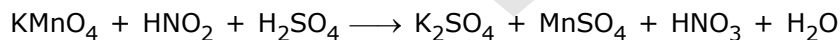


#### Properties :

(i) Oxidising property of  $\text{HNO}_2$



(ii) Reducing property of  $\text{HNO}_2$

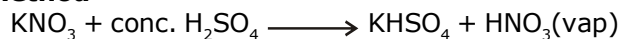


## NITRIC ACID (HNO<sub>3</sub>)

1. It was named aqua fortis (means strong water) by alchemists.

### Preparation

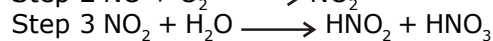
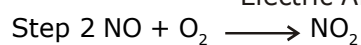
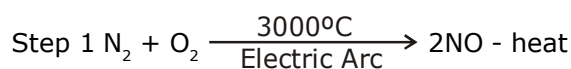
#### (i) Laboratory Method



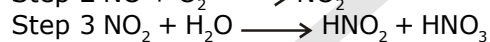
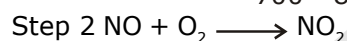
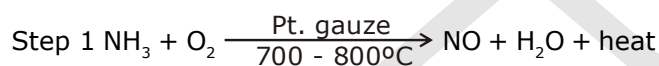
vapour of nitric acid evolved are condensed in a glass receiver.

#### (ii) Industrial Preparation

##### (A) Birkeland Eyde Process or arc process



##### (B) Ostwald's Process



### PROPERTIES

#### Physical

Nitric acid usually acquires yellow colour due to its decomposition by sunlight into NO<sub>2</sub>.

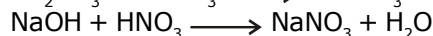
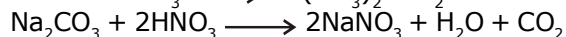
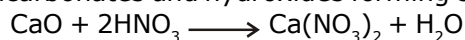


The yellow colour of the acid can be removed by warming it to 60–80°C and bubbling dry air through it.

It has extremely corrosive action on the skin and causes painful sores.

#### Chemical

(a) It is very strong acid. It exhibits usual properties of acids. It reacts with basic oxides, carbonates, bicarbonates and hydroxides forming corresponding salts.

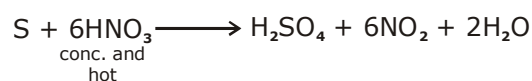


(b) **Oxidising nature :** Nitric acid acts as a strong oxidising agent as it decomposes to give nascent oxygen easily.



(i) **Oxidation of non-metals :** The nascent oxygen oxidises various non-metals to their corresponding highest oxyacids.

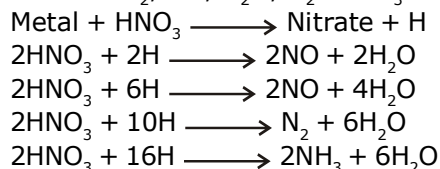
(1) Sulphur is oxidised to sulphuric acid







**(c) Action on Metals :** Most of the metals with the exception of noble metals like gold and platinum are attacked by Nitric acid. Nitric acid plays a double role in the action of metals, i.e., it acts as an acid as well as an oxidising agent. Armstrong postulated that primary action of nitric acid is to produce hydrogen in the nascent form. Before this hydrogen is allowed to escape, it reduces the nitric acid into number of products like  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$  or  $\text{NH}_3$  according to the following reactions :



The progress of the reaction is controlled by a number of factors :

- the nature of the metal
- the concentration of the acid
- the temperature of the reaction
- the presence of other impurities.

Concentration of nitric acid	Metal	Main Products
Very dilute $\text{HNO}_3$ (6%)	Mg, Mn	$\text{H}_2$ + Metal nitrate
	Fe, Zn, Sn	$\text{NH}_4\text{NO}_3$ + metal nitrate + $\text{H}_2\text{O}$
Dilute $\text{HNO}_3$ (20%)	Pb, Cu, Ag, Hg	$\text{NO}$ + metal nitrate + $\text{H}_2\text{O}$
	Fe, Zn	$\text{N}_2\text{O}$ + metal nitrate + $\text{H}_2\text{O}$
	Sn	$\text{NH}_4\text{NO}_3$ + $\text{Sn}(\text{NO}_3)_2$
Conc. $\text{HNO}_3$ (70%)	Zn, Fe, Pb, Cu, Ag	$\text{NO}_2$ + metal nitrate + $\text{H}_2\text{O}$
	Sn	$\text{NO}_2$ + $\text{H}_2\text{SnO}_3$ Metastannic acid

### Action on Proteins

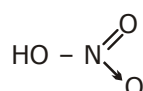
(i) Nitric acid attacks proteins forming a yellow nitro compound called xanthoprotein. It, therefore, stains skin and renders wool yellow colour. This property is utilized for the test of proteins.

(ii) **Oxidation** A number of organic compounds are oxidised.

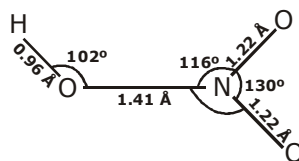
Sawdust catches fire when nitric acid is poured on it. Turpentine oil bursts into flames when treated with fuming nitric acid, Cane sugar is oxidised to oxalic acid. Toluene is oxidised to benzoic acid with dil.  $\text{HNO}_3$ .

### Structure

Nitric acid is a monobasic acid, i.e., the molecule consists of one hydroxyl group as it is formed by the hydrolysis of nitryl chloride,  $\text{NO}_2\text{Cl}$ . It may be structurally represented as below :

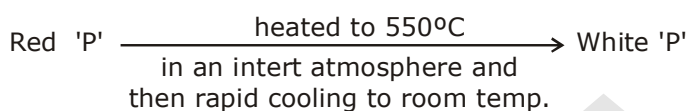
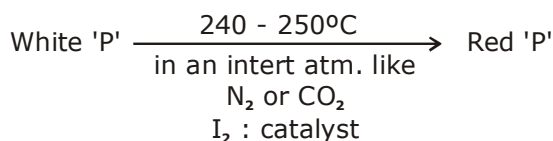


Gaseous nitric acid is a planar molecule. The bond lengths and bond angles as present in the molecule are represented in the figure :

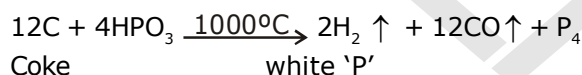
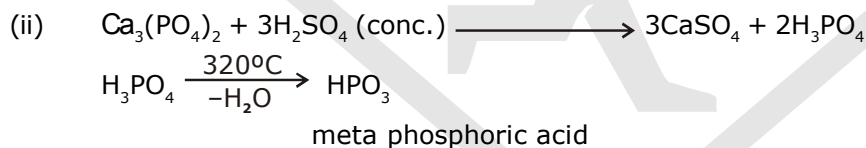
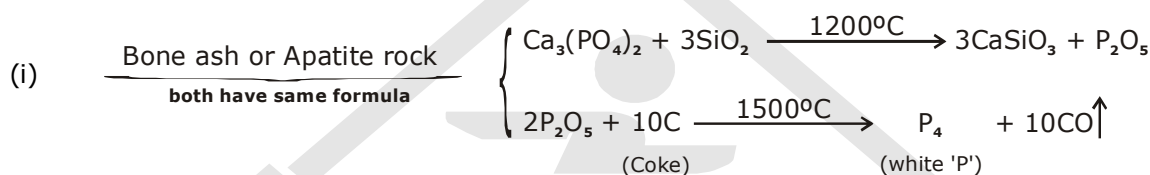


## PHOSPHOROUS

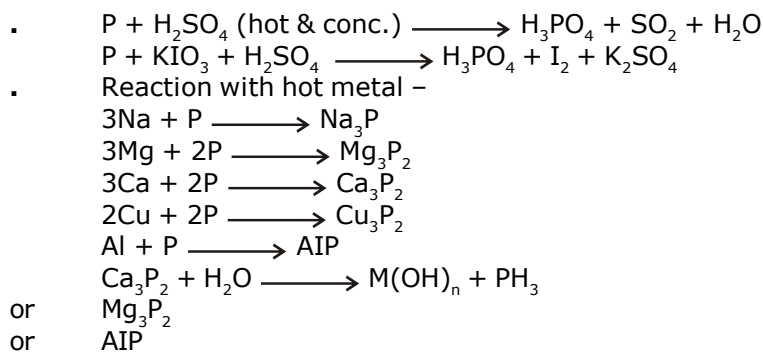
### INTERCONVERSION OF WHITE 'P' & RED 'P'

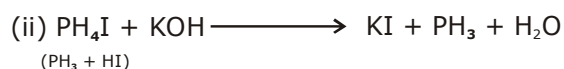


### PREPARATION OF WHITE 'P'

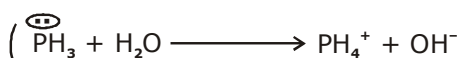
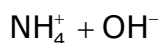


### REACTIONS OF 'P'



**PREPARATION OF PH<sub>3</sub> (PHOSPHINE GAS)**Purest PH<sub>3</sub>**PHYSICAL PROPERTIES**

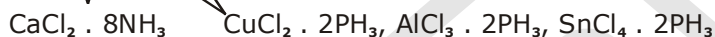
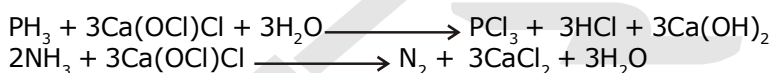
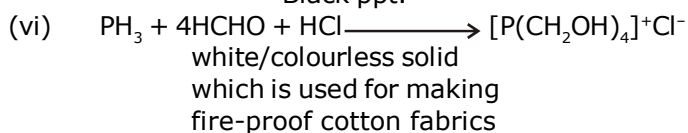
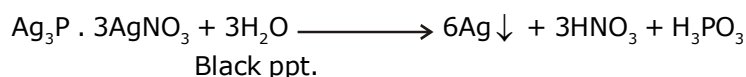
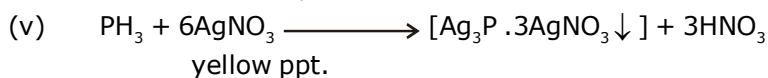
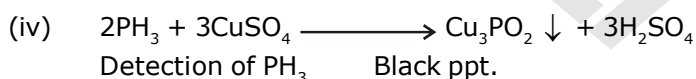
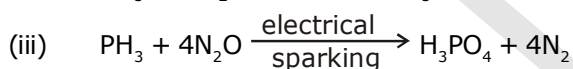
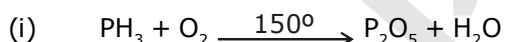
- (i) It is having rotten fish smell  
 (ii) It is soluble in CS<sub>2</sub> and insoluble in water.  
 (NH<sub>3</sub> is soluble in water)



→ in s-orbital, so donating capacity is less

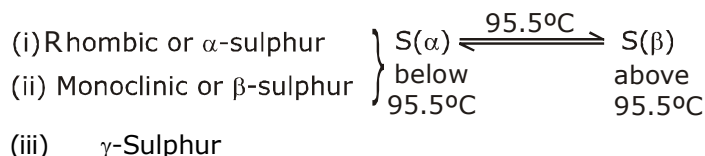
PH<sub>4</sub><sup>+</sup> is formed with acids

- (iii) Like NH<sub>3</sub>, PH<sub>3</sub> also can form addition product.

PH<sub>3</sub> can be absorbed by Ca(OCl)Cl.**OTHER REACTIONS OF PH<sub>3</sub>****EXAMPLE OF DEHYDRATING REACTION OF P<sub>2</sub>O<sub>5</sub>**

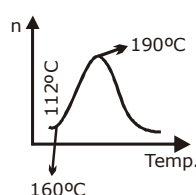
### GROUP VI SULPHUR CHEMISTRY

#### Allotropes :



#### Amorphous forms are

- (i) Plastic sulphur
- (ii) Milk of sulphur
- (iii) Colloidal sulphur



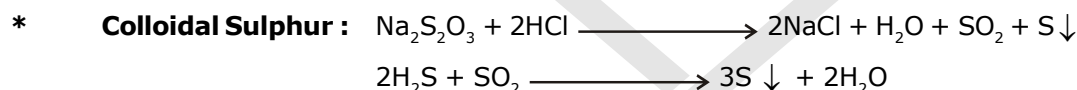
Viscosity of 'S' with temperature

m.p. of 'S'  $\longrightarrow$   $112.8^\circ\text{C}$

- (i)  $> 112.8^\circ\text{C}$  to  $160^\circ\text{C} \Rightarrow$  slow decrease due to  $\text{S}_8$  rings slip and roll over one another easily.
- (ii)  $> 160^\circ\text{C}$ , increases sharply due to breaking of  $\text{S}_8$  rings into chains and polymerises into large size chain.
- (iii)  $190^\circ\text{C}$ , again large chains are being broken into small chain.

#### \* Milk of sulphur :

Powdered 'S' +  $\text{Ca}(\text{OH})_2$  suspension  $\longrightarrow$  Solution  $\xrightarrow{\text{Acidified}}$  Milk of 'S'



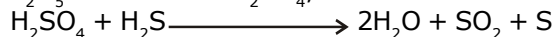
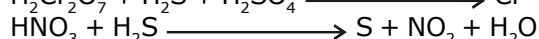
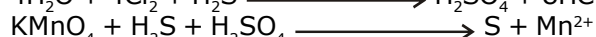
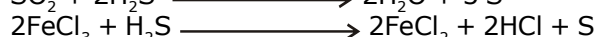
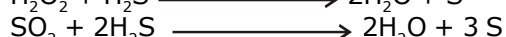
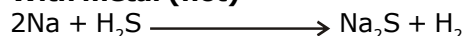
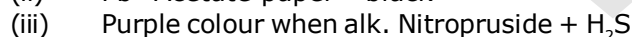
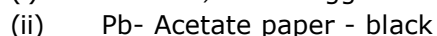
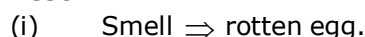
#### Props. of 'S'

- (a) Thin Cu-strip catches fire in sulphur vapour.  
 $\text{Cu} + \text{S} \longrightarrow \text{CuS}$ .
- (b) 'S' burns spontaneously in fluorine.  $\text{S} + 3\text{F}_2 \longrightarrow \text{SF}_6$   
 $\text{Cl}_2$  passed into liq. sulphur  $\Rightarrow 2 \text{S} + \text{Cl}_2 \longrightarrow \text{S}_2\text{Cl}_2$
- (c)  $\text{S} + 2\text{H}_2\text{SO}_4 \longrightarrow 3\text{SO}_2 + 2\text{H}_2\text{O}$   
 $\text{S} + 2\text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + 2\text{NO}$
- (d)  $4 \text{S} + 6 \text{KOH} \longrightarrow 2\text{K}_2\text{S} + \text{K}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$
- (e) Burns in air :  $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2$

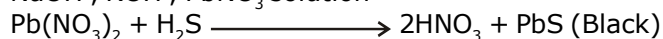
**H<sub>2</sub>S :****Prep<sup>n</sup> :**

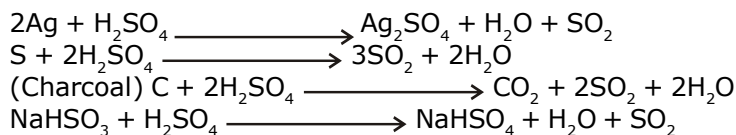
Drying agent for this gas : fused CaCl<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> (dehydrated)

P<sub>2</sub>O<sub>5</sub> etc. But not H<sub>2</sub>SO<sub>4</sub>, because

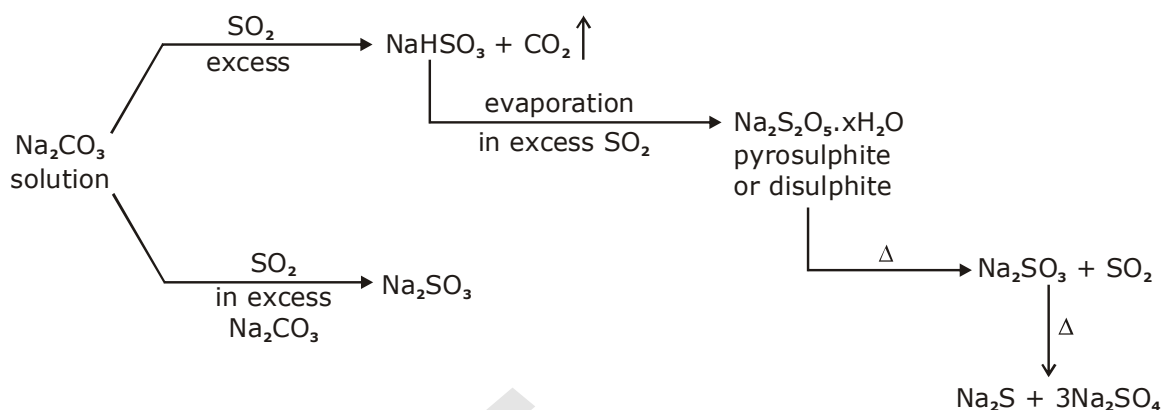
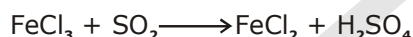
**Reducing property of H<sub>2</sub>S :****With metal (hot)****With metal oxide (hot)****Test :****Absorbent :**

NaOH, KOH, PbNO<sub>3</sub> solution

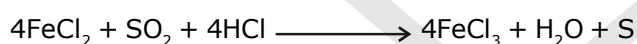
**SO<sub>2</sub>****Prep :****Industrial :****Lab prep<sup>n</sup> :**

**Props :**

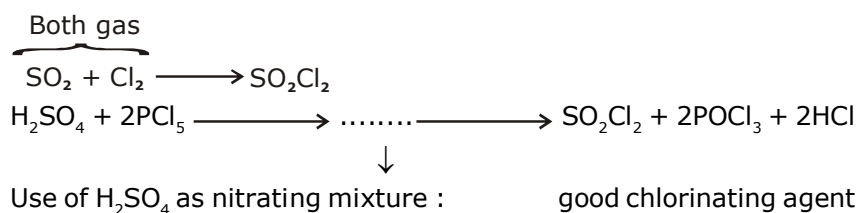
- (i) Incombustible gas, but heated K burns in  $\text{SO}_2$   
 $4\text{K} + 3\text{SO}_2 \longrightarrow \text{K}_2\text{SO}_3 + \text{K}_2\text{S}_2\text{O}_3$

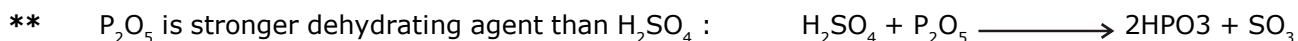
**Reducing Prop.:** (Revise from acid radical)

Add HCl  
to make  
strongly  
acidic and  
 $\text{SO}_2$   
passed

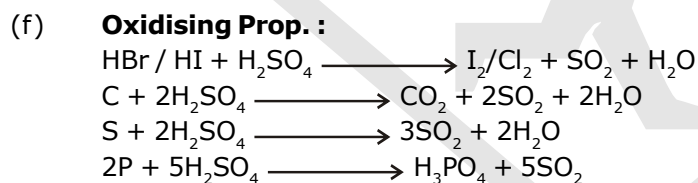
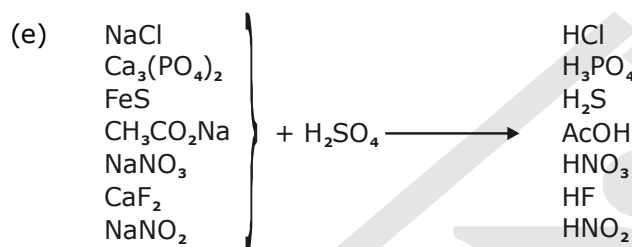
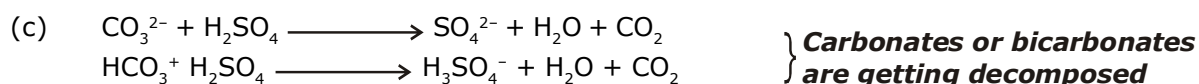
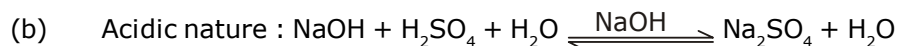
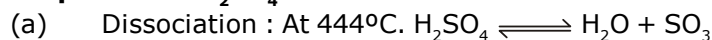


- (ii)  $\text{SO}_2 + 2\text{H}_2\text{SO}_3 \xrightarrow[\text{sealed tube}]{150^\circ\text{C}} 2\text{H}_2\text{SO}_4 + \text{S}$   
 $\text{FeSO}_4 \longrightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$   
 $\text{Fe}_2(\text{SO}_4)_3 \longrightarrow \text{Fe}_2\text{O}_3 + 3\text{SO}_3$

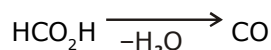
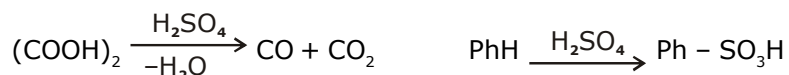
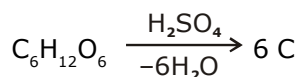
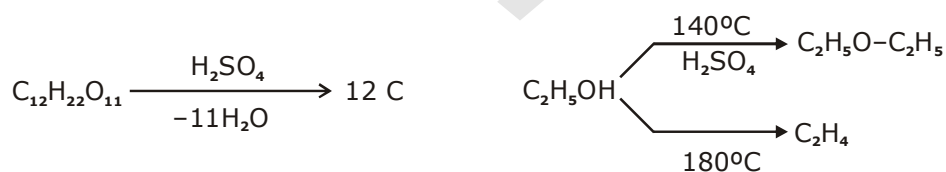
 **$\text{H}_2\text{SO}_4$  &  $\text{SO}_3$  :**

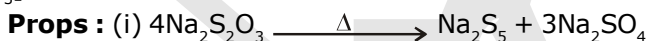
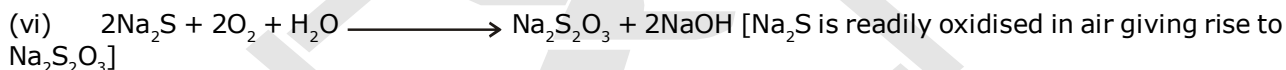
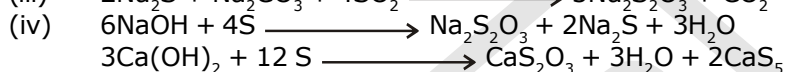
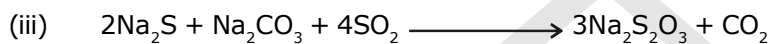
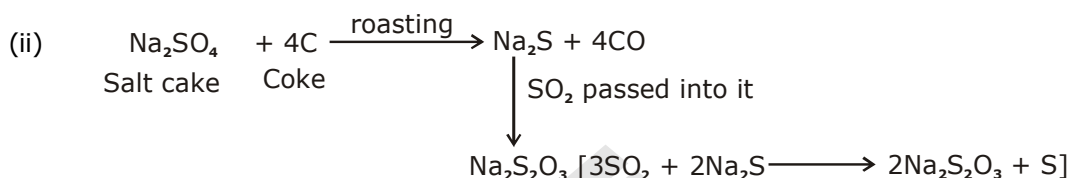
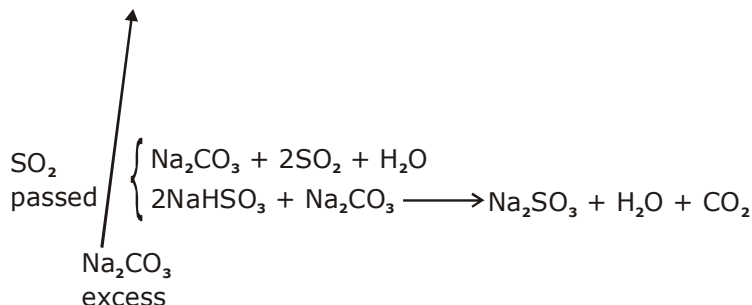
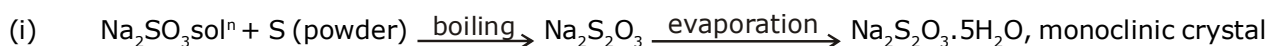
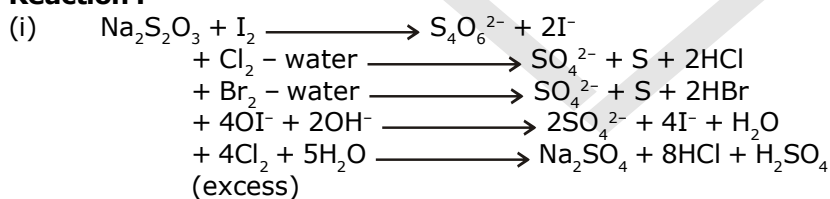


**Properties of  $H_2SO_4$  :**



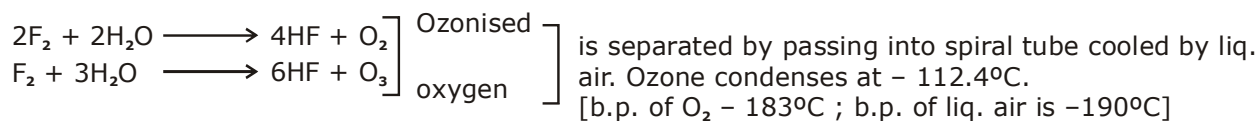
(g) Dehydrating agent :



**SODIUM THIOSULPHATE****Prep<sup>n</sup> :****Reaction :****OZONE**

$\Rightarrow$  Unstable deep blue, diamagnetic gas, with fishy smell. Toxic enough (more toxic than KCN). Its intense blue colour is due to the absorption of red light.

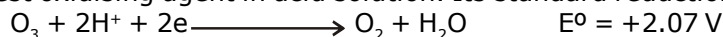
$\Rightarrow$





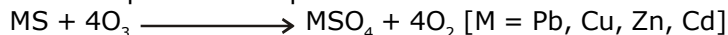
⇒ **Oxidising property of O<sub>3</sub>**

It is one of best oxidising agent in acid solution. Its standard reduction potential value is 2.07 V.



It is next to F<sub>2</sub>. [above 2.07 V, only F<sub>2</sub>, F<sub>2</sub>O are there]

(i) Metal Sulphides to Sulphates.

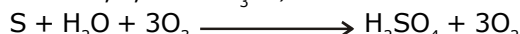


(ii)  $2\text{HX} + \text{O}_3 \longrightarrow \text{X}_2 + \text{H}_2\text{O} + \text{O}_2$  [X = Cl, Br, I]

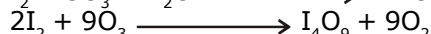
(iii)  $\text{NaNO}_2 + \text{O}_3 \longrightarrow \text{NaNO}_3 + \text{O}_2$



(iv) Moist S, P, As + O<sub>3</sub> ⇒



(v) Moist I<sub>2</sub>  $\longrightarrow$  HIO<sub>3</sub> whereas dry iodine  $\longrightarrow$  I<sub>4</sub>O<sub>9</sub> (yellow)



(vi)  $2\text{K}_2\text{MnO}_4 + \text{O}_3 + \text{H}_2\text{O} \longrightarrow 2\text{KMnO}_4 + 2\text{KOH} + \text{O}_2$



(vii)(a)  $2\text{KI} (\text{acidified}) + \text{O}_3 + 2\text{HCl} \longrightarrow \text{I}_2 + 2\text{KCl} + \text{H}_2\text{O} + \text{O}_2$

(b)  $2\text{KI} (\text{neutral}) + \text{O}_3 + \text{H}_2\text{O} \longrightarrow$

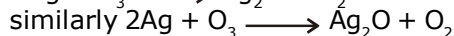


O<sub>3</sub> estimated by this reaction



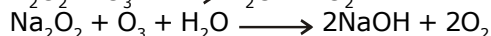
(c) alk.  $\begin{cases} \text{KI} + 3\text{O}_3 \longrightarrow \text{KIO}_3 + 3\text{O}_2 \\ \text{KI} + 4\text{O}_3 \longrightarrow \text{KIO}_4 + 4\text{O}_2 \end{cases}$

(viii) Hg loses its fluidity (tailing of Hg)



Brown

(ix)  $\text{BaO}_2 + \text{O}_3 \longrightarrow \text{BaO} + 2\text{O}_2$



(x)  $2\text{KOH} + 5\text{O}_3 \longrightarrow 2\text{KO}_3 + 5\text{O}_2 + \text{H}_2\text{O}$

**In all above reaction O<sub>3</sub> gives up O<sub>2</sub> but some reactions are there which consumes all O-atom**

(i)  $3\text{SO}_2 + \text{O}_2 \longrightarrow 3\text{SO}_3$

(ii)  $3\text{SnCl}_2 + 6\text{HCl} + \text{O}_3 \longrightarrow 3\text{SnCl}_4 + 3\text{H}_2\text{O}$

**Absorbent :**

- (i) Turpentine oil
- (ii) Oil of cinnamon

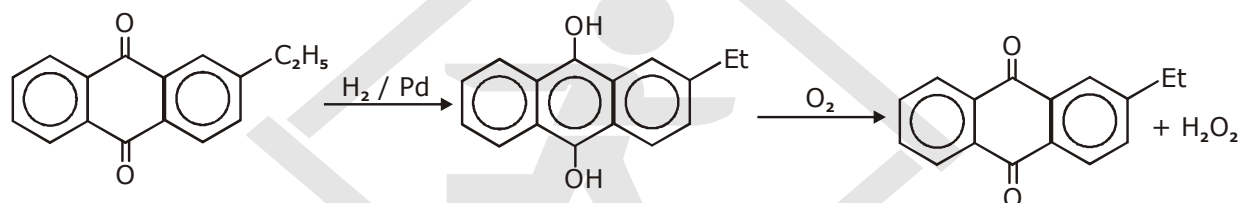
**test :**

- (i) Sterilising water
- (ii) Detection of position of the double bond in the unsaturated compound.

**Method preparation :**

- (i)  $\text{Na}_2\text{O}_2 + \text{H}_2\text{O (ice cold water)} \longrightarrow 2\text{NaOH} + \text{H}_2\text{O}_2$
- (ii)  $\text{BaO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$   
Instead of  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$  is added now - a - days because  $\text{H}_2\text{SO}_4$  catalyses the decomposition of  $\text{H}_2\text{O}_2$  whereas  $\text{H}_3\text{PO}_4$  favours to restore it.  
 $3\text{BaO}_2 + 2\text{H}_3\text{PO}_4 \longrightarrow \text{Ba}_3(\text{PO}_4)_2 + 3\text{H}_2\text{O}_2$  and  $\text{Ba}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 \longrightarrow 3\text{BaSO}_4 + 2\text{H}_3\text{PO}_4$  (reused again)
- (iii) Electrolysis of 50%  $\text{H}_2\text{SO}_4$  using high current density.  
 $2\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{H}^+ + 2\text{HSO}_4^-$   
 $2\text{HSO}_4^- \longrightarrow \text{H}_2\text{S}_2\text{O}_8 + 2\text{e}^-$  [At anode] [At cathode  $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$ ]  
 $\text{H}_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} \longrightarrow 2\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$

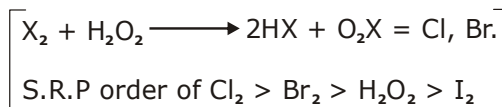
(iv)

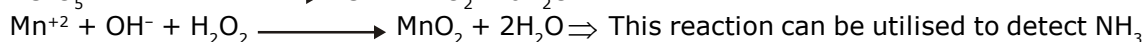
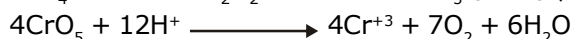
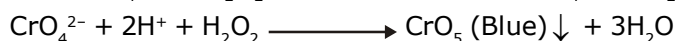
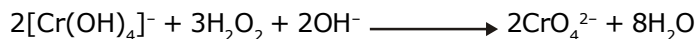
**Properties :**

- (i) Colourless, odourless liquid (b.p.  $152^\circ$ )
- (ii) Acidic nature :  
 $\text{H}_2\text{O}_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{O}_2 + \text{H}_2\text{O}$   
 $\text{H}_2\text{O}_2 + \text{Ba}(\text{OH})_2 \longrightarrow \text{BaO}_2 + 2\text{H}_2\text{O}$   
 $\text{H}_2\text{O}_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{Na}_2\text{O}_2 + \text{CO}_2 + \text{H}_2\text{O}$
- (iii) It is oxidant as well as reductant.  
 $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow 2\text{H}_2\text{O}$  [reaction in acidic medium]  
 $\text{H}_2\text{O}_2 + 2\text{e}^- \longrightarrow 2\text{OH}^-$  [reaction in alkali medium]

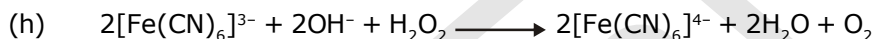
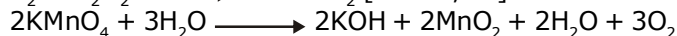
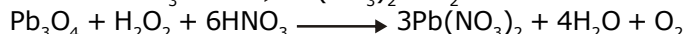
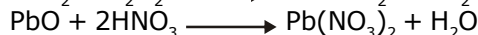
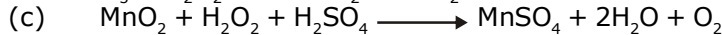
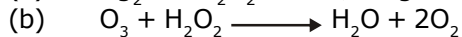
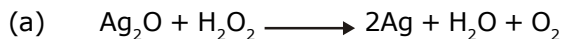
**Oxidising Properties :**

- (i)  $\text{PbS} + 4\text{H}_2\text{O}_2 \longrightarrow \text{PbSO}_4 + 4\text{H}_2\text{O}$  ( Used in washing of oil painting)
- (ii)  $\text{NaNO}_2 + \text{H}_2\text{O}_2 \longrightarrow \text{NaNO}_3 + \text{H}_2\text{O}$   
 $\text{Na}_2\text{SO}_3 + \text{H}_2\text{O}_2 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$   
 $\text{Na}_3\text{AsO}_3 + \text{H}_2\text{O}_2 \longrightarrow \text{Na}_3\text{AsO}_4 + \text{H}_2\text{O}$   
 $2\text{KI} + \text{H}_2\text{O}_2 \longrightarrow 2\text{KOH} + \text{I}_2$   
 $\text{H}_2\text{S} + \text{H}_2\text{O}_2 \longrightarrow \text{S} \downarrow + 2\text{H}_2\text{O}$   
 $\text{H}_2\text{SO}_4 + 2\text{FeSO}_4 + \text{H}_2\text{O}_2 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}$   
 $2\text{K}_4[\text{Fe}(\text{CN})_6] + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \longrightarrow 2\text{K}_3[\text{Fe}(\text{CN})_6] + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$





**Reducing properties :**



**Uses :**

(i) As a rocket propellant :



(ii) In detection of  $\text{Cr}^{+3}$ ,  $\text{Ti}^{+4}$  etc.



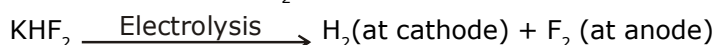
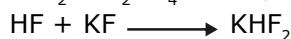
Yellow or orange

Pertitanic acid

### GROUP - VII HALOGENS

**Method of Prep" :**

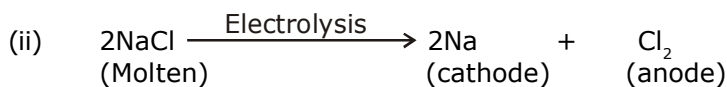
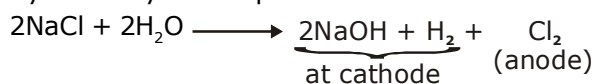
**F<sub>2</sub> :** By electrolysis of  $\text{KHF}_2$  (which is obtained from  $\text{CaF}_2$ )

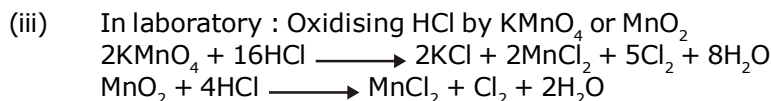


**{ KF decrease the m.p. of  
the mix. depending upon  
the composition. }**

**Cl<sub>2</sub> :**

(i) By electrolysis of aq. NaCl





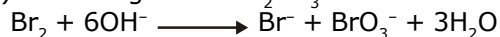
**$\text{Br}_2$**  : From Bromine water (contains 65 ppm of  $\text{Br}^-$ )



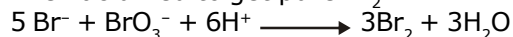
Hence it is collected by

(i) removal of  $\text{Br}_2$  vapour by stream of air.

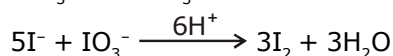
(ii) absorbing it into  $\text{Na}_2\text{CO}_3$  solution.



Then acidified to get pure  $\text{Br}_2$



**$\text{I}_2$**  : Chille salt petre contains traces of  $\text{NaIO}_3$  which is reduced to  $\text{I}^-$  by  $\text{NaHSO}_3$ , then oxidation of  $\text{I}^-$  to  $\text{I}_2$  by  $\text{IO}_3^-$ .



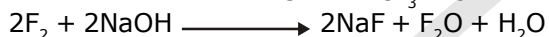
Q. Liquid  $\text{I}_2$  conducts electricity. Explain

Ans. Due to its self ionisation  $3\text{I}_2 \longrightarrow \text{I}_3^+ + \text{I}_3^-$

Q.  $\text{X}_2 + \text{OH}^- \longrightarrow \text{X}^- + \text{OX}^- + \text{H}_2\text{O}$  but on acidification the disproportionated product gives back the same element.



$\text{X}_2 = \text{Cl}_2, \text{Br}_2, \text{I}_2$  But For  $\text{F}_2$



$\text{X} = \text{Cl}, \text{Br}, \text{I}$

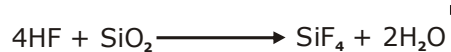
### HALOGEN ACID :

Acidity order :  $\text{HI} > \text{HBr} > \text{HCl} \gg \text{HF}$ . (due to hydrogen bonding & less effective overlap with H atom)

Q.  $\text{CaF}_2$  used in HF prep<sup>n</sup> must be free from  $\text{SiO}_2$ . Explain

Ans.  $\text{CaF}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + \text{HF}$

If  $\text{SiO}_2$  present as impurity

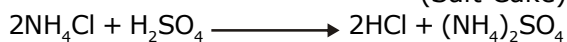
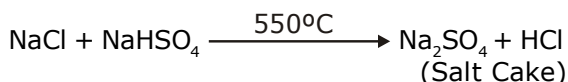
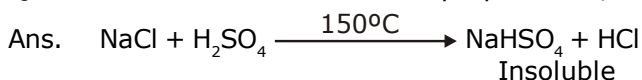


Hence presence of one molecule  $\text{SiO}_2$

consumer 6 molecule of HF

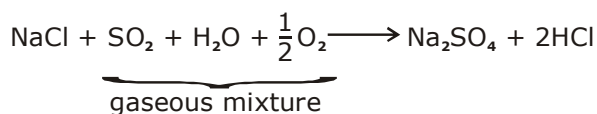
Q. HF can not be stored in glass vessel. Explain. (same reason.)

Q. In the salt-cake method of prep<sup>n</sup>. of HCl,  $\text{NH}_4\text{Cl}$  is being used instead of  $\text{NaCl}$ . Explain.



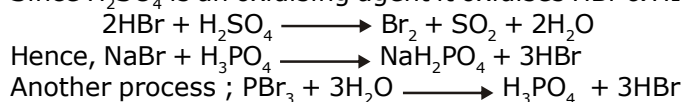
[ $\text{NH}_4\text{HSO}_4$  intermediate is water soluble and easy to handle]

\*\* Another alternative process to avoid the formation of  $\text{NaHSO}_4$



Q. In the similar type of preparation of  $\text{HBr}$  and  $\text{HI}$  from bromide and iodide,  $\text{H}_2\text{SO}_4$  can not be used and  $\text{H}_3\text{PO}_4$  is used. Explain.

Ans. Since  $\text{H}_2\text{SO}_4$  is an oxidising agent it oxidises  $\text{HBr}$  &  $\text{HI}$  to  $\text{Br}_2$  and  $\text{I}_2$  respectively.



Q. Boiling point order  $\text{HX}$  :  $\text{HF} > \text{HI} > \text{HBr} > \text{HCl}$

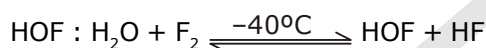
↓  
Due to H-bonding

Q.  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  are bases in liquid  $\text{HF}$  where as  $\text{HClO}_4$  is acid. Comment.

Ans.  $\text{HCl} + \text{HF} \longrightarrow \text{H}_2\text{Cl}^+ + \text{F}^-$  ;  $\text{H}_2\text{SO}_4 + \text{HF} \longrightarrow \text{H}_3\text{SO}_4^+ + \text{F}^-$  ;  $\text{HNO}_3 + \text{HF} \longrightarrow \text{H}_2\text{NO}_3^+ + \text{F}^-$   
But  $\text{HClO}_4 + \text{HF} \longrightarrow \text{H}_2\text{F}^+ + \text{ClO}_4^-$

\*  $\text{HF}$  is weak acid but addition of  $\text{BF}_3$ ,  $\text{AsF}_5$ ,  $\text{PF}_5$ ,  $\text{SbF}_5$  makes it strongly acidic. Explain

### OXOACIDS :

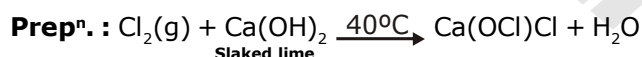


**HOX** : very unstable because  
it reacts with both  $\text{H}_2\text{O}$   
and  $\text{F}_2$  as follows :

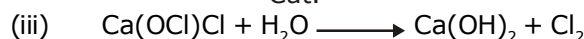
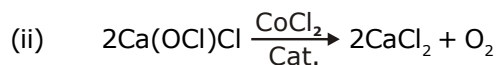
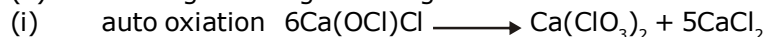


$\text{OX}^-$  disproportionates in hot solution eg.  $3\text{OCl}^- \longrightarrow 2\text{Cl}^- + \text{ClO}_3^-$   
 $\text{X} = \text{Cl}, \text{Br}, \text{I}$

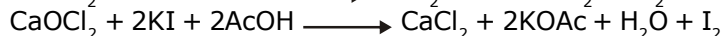
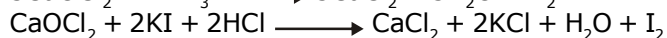
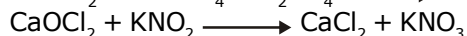
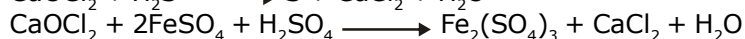
**Bleaching Powder** :  $\text{Ca} \begin{array}{l} \text{Cl} \\ \text{OCl} \end{array}$

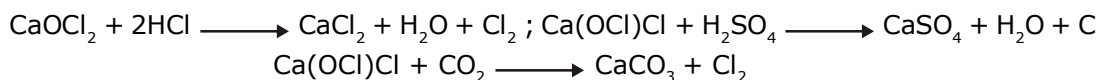
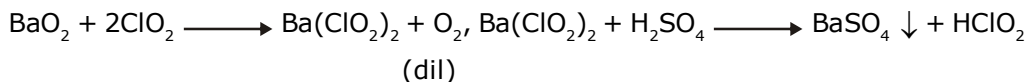


(a) On long standing it undergoes



### Oxidising Prop :

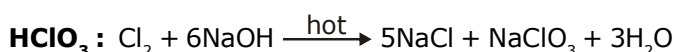


**Reaction with acid :****HXO<sub>2</sub> :**

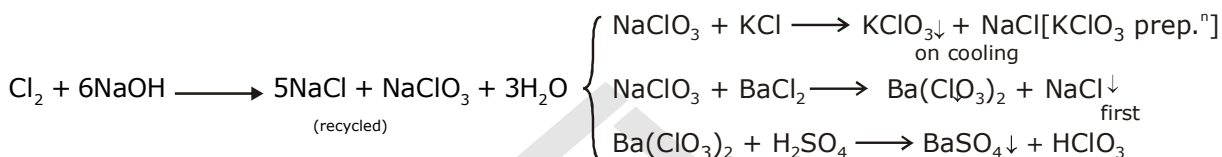
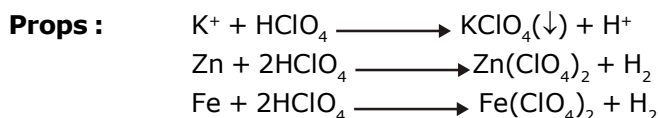
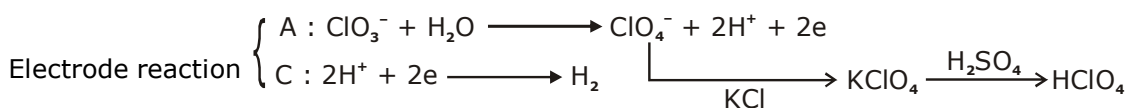
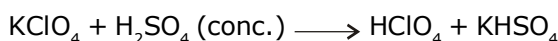
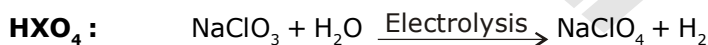
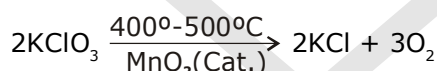
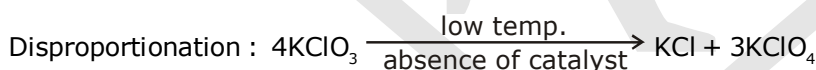
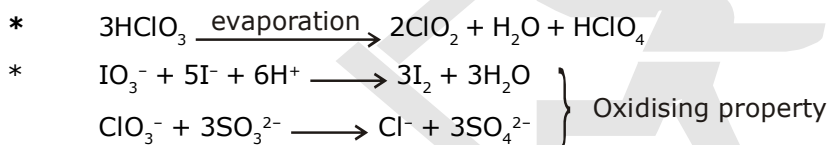
Only Known HClO<sub>2</sub>. It is stable in alkaline solution but disproportionates in acid solution.



**HXO<sub>3</sub> :** HClO<sub>3</sub> > HBrO<sub>3</sub> > HIO<sub>3</sub> are known and acidic order is as shown

**Prep<sup>n</sup>:**

Similarly electrolysis of hot halide solution with severe stirring gives the same product.

**Properties :**

Acidity order :  $\text{HOX} < \text{HXO}_2 < \text{HXO}_3 < \text{HXO}_4$

Oxidising power :  $\text{HOX} > \text{HXO}_2 > \text{HXO}_3 > \text{HXO}_4$

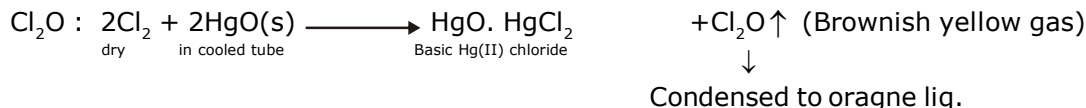
Thermal stability :  $\text{HOX} < \text{HXO}_2 < \text{HXO}_3 < \text{HXO}_4$

**OXIDES OF CHLORINE**

+1	+4	+6	+7
Cl <sub>2</sub> O	ClO <sub>2</sub>	Cl <sub>2</sub> O <sub>6</sub>	Cl <sub>2</sub> O <sub>7</sub>
(Brownish yellow)	(Pale yellow)	(liq. – dark red solid – yellow) solid	colourless

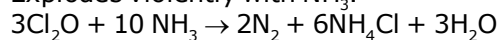
**Prep<sup>n</sup> :**

Cl<sub>2</sub> does not combine directly to produce its oxides but indirect methods are there.

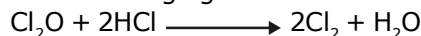
**Props :**

It dissolves in water :  $\text{Cl}_2\text{O} + \text{H}_2\text{O} \longrightarrow 2\text{HClO}$

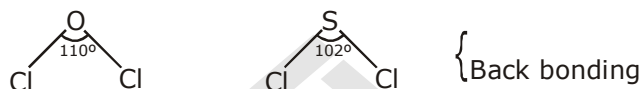
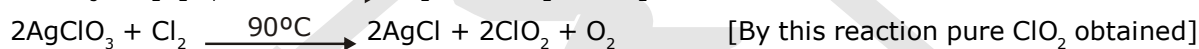
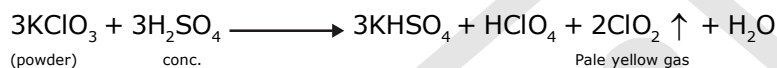
Explodes violently with NH<sub>3</sub>.



It is oxidising agent

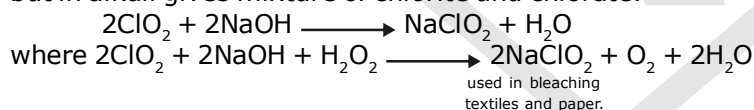


Structures :

**ClO<sub>2</sub> : Prep<sup>n</sup> :**

ClO<sub>2</sub> dissolves in water  
 $\text{ClO}_2 \longrightarrow \text{ClO} + \text{O}$   
 producing dark green 2ClO + H<sub>2</sub>O  $\longrightarrow$  HCl + HClO<sub>3</sub>  
 solution which decomposes  
 in presence of light.

but in alkali gives mixture of chlorite and chlorate.

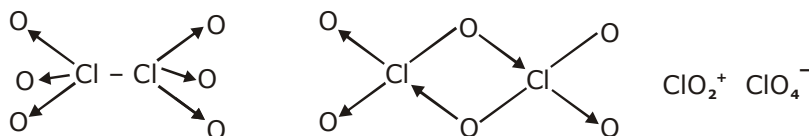


ClO<sub>2</sub> does not dimerise because odd e<sup>-</sup>s undergoes delocalisation (in its own vacant 3d-orbital)

Cl<sub>2</sub>O<sub>4</sub> (Cl<sub>2</sub>.ClO<sub>4</sub>) is not the dimer of ClO<sub>2</sub>. Actually it is Cl-perchlorate.

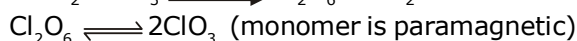
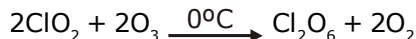


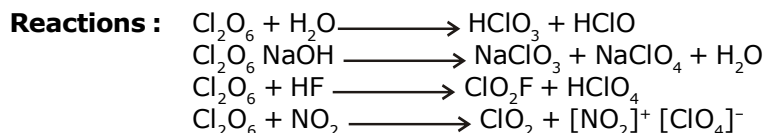
**Cl<sub>2</sub>O<sub>6</sub> :** Possible structures are :



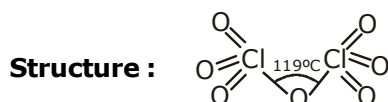
liq  $\longrightarrow$  dark red  
 Solid  $\longrightarrow$  Yellow

Q. Prove that Cl<sub>2</sub>O<sub>6</sub> is consisting ClO<sub>2</sub><sup>+</sup> and ClO<sub>4</sub><sup>-</sup>

**Prep<sup>n</sup> :**



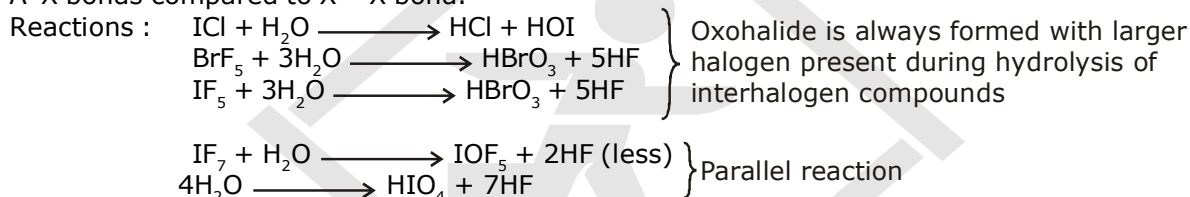
**Cl<sub>2</sub>O<sub>7</sub>** (colourless solid) : It is the anhydride of HClO<sub>4</sub> and prepared from it by the action P<sub>2</sub>O<sub>5</sub>.  
 $2\text{HClO}_4 + \text{P}_2\text{O}_5 \rightarrow 2\text{HPO}_3 + \text{Cl}_2\text{O}_7$



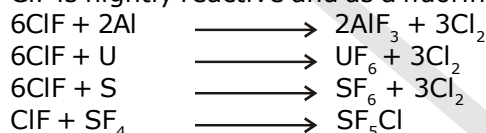
### INTER HALOGEN

Types :	AX	AX <sub>3</sub>	AX <sub>5</sub>	AX <sub>7</sub>
	ClF	ClF <sub>3</sub>	ClF <sub>5</sub>	IF <sub>7</sub>
	BrF	BrF <sub>3</sub>	BrF <sub>5</sub>	
	BrCl	(ICl <sub>3</sub> ) <sub>2</sub>	IF <sub>5</sub>	
	ICl	IF <sub>3</sub> (unstable)		
	IBr			
	IF (unstable)			

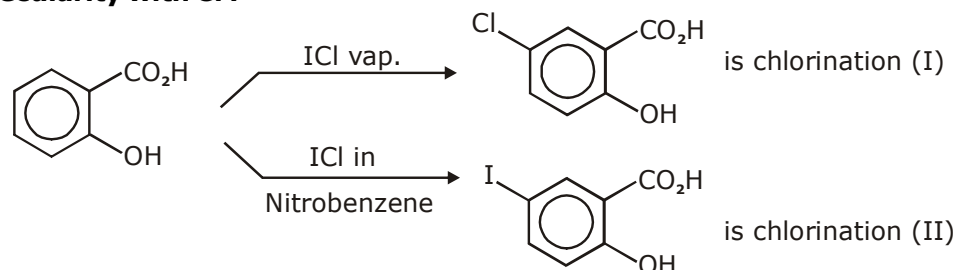
- \*  $5\text{IF} \longrightarrow \text{IF}_5 + 2\text{I}_2$  [The overall system gains B.E. by 250 kJ/mol]
- \* There are never more than two halogens in a molecule.
- \* bonds are essentially covalent and b.p. increases as the E.N. difference increases.
- \* AX<sub>5</sub> & AX<sub>7</sub> type formed by large atoms like Br & I to accommodate more atoms around it.
- \* The interhalogens are generally more reactive than the halogens (except F<sub>2</sub>) due to weaker A-X bonds compared to X-X bond.



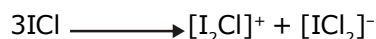
(i) ClF is highly reactive and as a fluorinating agent.



**One peculiarity with Cl :**



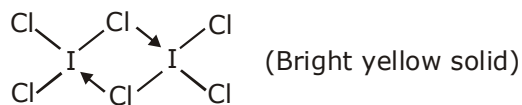
In IIInd case, the attacking species is I<sup>+</sup> which has been supported by the formation of I<sup>+</sup> in fuse state as follows :



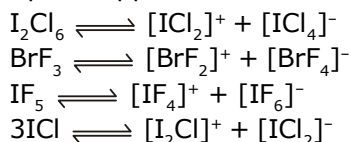
\* ICl<sub>3</sub> does not exist



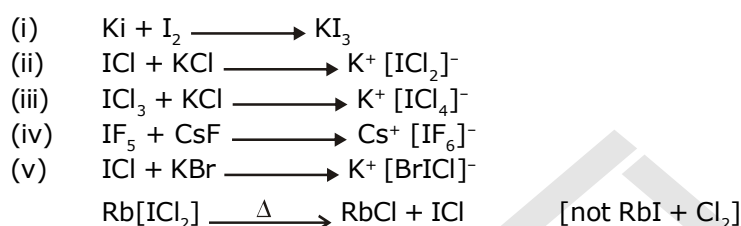
but its dimer exist.  $\rightleftharpoons 2\text{ICl}_3 \rightleftharpoons \text{I}_2\text{Cl}_6$   
 Structure is planar.



$\text{I}_2\text{Cl}_6$  : liq. has appreciable electrical conductivity like other interhalogens.

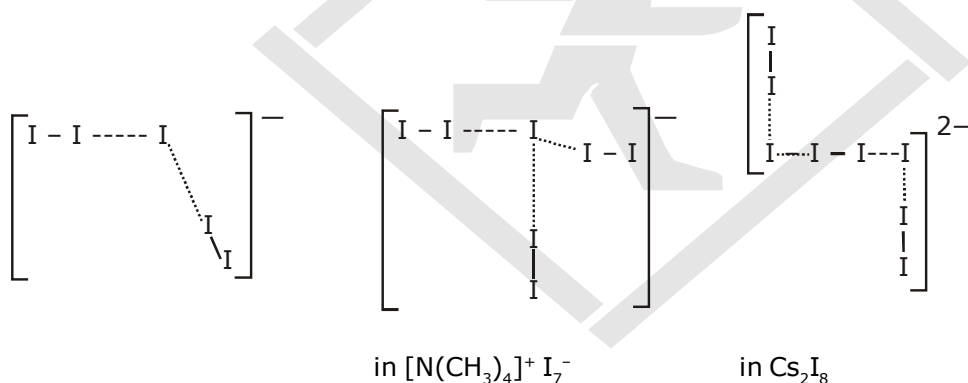


### Polyhalides :



Here the products on heating depends on the lattice energy of the product halide. The lattice energy of alkali halide with smaller halogen is highest since the interatomic distance is least.

Structure of  $\text{I}_5^-$ ,  $\text{I}_7^-$ ,  $\text{I}_8^{2-}$



- \* Only  $\text{F}_3^-$  not known [due to absence of d-orbital] [i.e.  $\text{Cs}_2\text{I}_3 - \text{I}_2 - \text{I}_3$ ]  
 $\text{I}_3^-$ ,  $\text{Br}_3^-$ ,  $\text{Cl}_3^-$  are known  $\text{Cl}_3^-$  compounds are very less.  
 Stability order :  $\text{I}_3^- > \text{Br}_3^- > \text{Cl}_3^-$  : depends upon the donating ability of  $\text{X}^-$ .

### PSEUDO HALOGEN

There are univalent ion consisting of two or more atoms of which at least one is N, that have property similar to those of the halide ions. E.g.

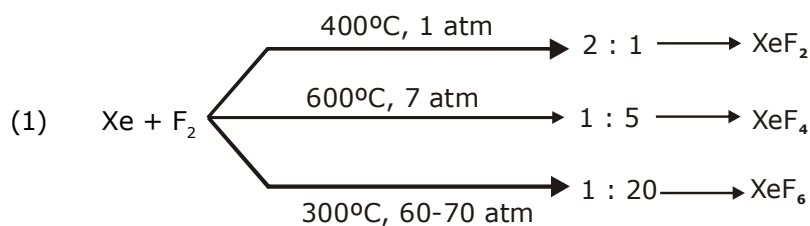
- Na-salts are soluble in water but Ag-salts are insoluble in water.
- H-compounds are acids like HX.
- some anions can be oxidised to give molecules  $\text{X}_2$ .

Anions :	Acids	Dimer
CN <sup>-</sup>	HCN	(CN) <sub>2</sub>
SCN <sup>-</sup>	HSCN(thiocyanic acid)	(SCN) <sub>2</sub>
SeCN <sup>-</sup>		(SeCN) <sub>2</sub>
OCN <sup>-</sup>	HOCN (cyanic acid)	
NCN <sup>2-</sup> (Bivalent)	H <sub>2</sub> NCN(cyanamide)	
ONC <sup>-</sup>	HONC (Fulminic acid)	
N <sub>3</sub> <sup>-</sup>	HN <sub>3</sub> (Hydrazoic acid)	
CN <sup>⊖</sup> shows maximum similarities with Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup>		
(i)	forms HCN	
(ii)	forms (CN) <sub>2</sub>	
(iii)	AgCN, Pb(CN) <sub>2</sub> , are insoluble	
(iv)	Inter pseudo halogen compounds ClCN, BrCN, ICN can be formed	
(v)	AgCN is insoluble in H <sub>2</sub> O but soluble in NH <sub>3</sub>	
(vi)	forms large no. of complex e.g.	[Cu(CN) <sub>4</sub> ] <sup>3-</sup> & [CuCl <sub>4</sub> ] <sup>-3</sup> [Co(CN) <sub>6</sub> ] <sup>-3</sup> & [CoCl <sub>6</sub> ] <sup>-3</sup>

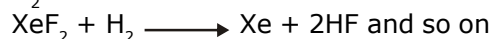
**NOBLE GASES**

- \* I.E. order : He > Ne > Ar > Kr > Xe > Rn
- \* M.P. order : He < Ne < Ar < Kr < Xe < Rn
- ↓
- \* B.P. order : (-269°C) same
- \* Atomic radius order : Same
- \* Density order : Same
- \* Relative abundance : Ar is highest (Ne, Kr, He, Rn)
- "He" (helium) has the lowest b.p (-269°C) of any liquid (lowest of any substance)
- (i) It is used in cryoscopy to obtain the very low temperature required for superconductor and laser.
- (ii) It is used in airships though H<sub>2</sub> is cheaper and has lower density compared to He because H is highly inflammable.
- (iii) He is used in preference to N<sub>2</sub> to dil. O<sub>2</sub> in the gas cylinders used by divers. This is because N<sub>2</sub> is quite soluble in blood, so a sudden change in pressure causes degassing and gives bubbles of N<sub>2</sub> in the blood. This causes the painful condition called bends.
- He is slightly soluble so the risk of bends is reduced.
- \* Noble gases are all able to diffuse through glass, rubber, plastics and some metals
- \* He liquid can exist in two forms . I-form when changes to II-form at λ-point temperature many physical properties change abruptly.
- e.g.
- (i) Sp. heat changes by a factor of 10
- (ii) Thermal conductivity increases by 10<sup>6</sup> and it becomes 800 times faster than Cu
- (iii) It shows zero resistance
- (iv) It can flow up the sides of the vessel
- \* Ar, Kr, Xe can form clathrate compounds but He, Ne cannot due to their smaller size.
- What is noble gas hydrate ?
- e.g.
 

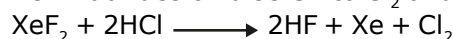
Xe . 6H <sub>2</sub> O	{	formed only when
Ar . 6H <sub>2</sub> O		water freezes at high
Kr . 6H <sub>2</sub> O		pressure together with noble gas

**Xenon Fluorides :-**

(2)  $\text{H}_2$  reduces Xe - fluorides to Xe

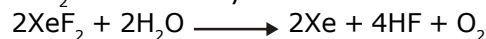


(3) Xe - fluorides oxidise  $\text{Cl}^-$  to  $\text{Cl}_2$  and  $\text{I}^-$  to  $\text{I}_2$

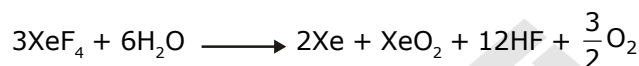


(4) Hydrolysis

$\text{XeF}_2$  reacts slowly with water



$\text{XeF}_4$  and  $\text{XeF}_6$  react violently with water giving  $\text{XeO}_3$



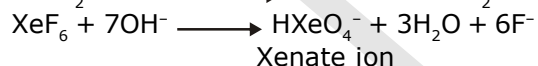
↓

(explosive, white hygroscopic solid)

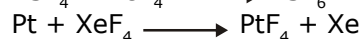
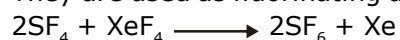
(5)  $\text{SiO}_2$  also converts  $\text{XeF}_6$  into  $\text{XeOF}_4$



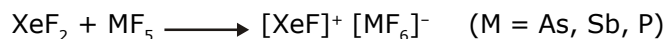
(6) Xe - fluorides are also hydrolysed in alkaline medium.



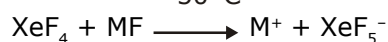
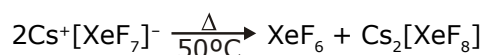
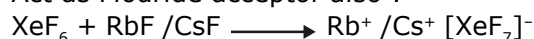
(7) They are used as fluorinating agent



(8) Act as a fluoride donor



(9) Act as Fluoride acceptor also :

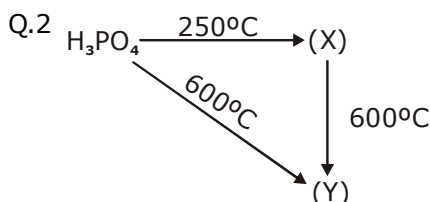


(alkali metals fluoride)

**EXERCISE – I****OBJECTIVE PROBLEMS (JEE MAIN)****ONLY ONE OPTION IS CORRECT**

Q.1 Which is incorrectly matched ?

- (A)  $\text{CsBr}_3 \rightleftharpoons \text{Cs}^+ + \text{Br}_3^-$   
 (B)  $\text{I}_4\text{O}_9 \rightleftharpoons \text{I}^{3+} + (\text{IO}_3^-)_3$   
 (C)  $\text{AgBrO}_3 \rightleftharpoons \text{Ag}^+ + \text{BrO}_3^-$   
 (D)  $\text{I}_2\text{O}_4 \rightleftharpoons \text{IO}_2^- + \text{IO}_2^+$

**Sol.**

- (A) (X) = Pyrophosphoric acid (liquid),  
 (Y) = Metaphosphoric acid (liquid)  
 (B) (X) = Pyrophosphoric acid (liquid),  
 (Y) = Metaphosphoric acid (Solid)  
 (C) (X) = Pyrophosphoric acid (solid),  
 (Y) = Metaphosphoric acid (solid)  
 (D) (X) = Pyrophosphoric acid (solid),  
 (Y) = Metaphosphoric acid (liquid)

**Sol.**Q.3  $\text{H}_3\text{PO}_2 \xrightarrow{\Delta} (\text{X}) + \text{PH}_3$  ; is

- (A) Dehydration reaction  
 (B) Oxidation reaction  
 (C) Disproportionation reaction  
 (D) Dephosphorylation reaction

**Sol.**

Q.4 Which of the following species is not a pseudohalide ?

- (A)  $\text{CNO}^-$  (B)  $\text{RCOO}^-$   
 (C)  $\text{OCN}^-$  (D)  $\text{N}_3^-$

**Sol.**

Q.5 An orange solid (X) on heating, gives a colourless gas (Y) and a only green residue (Z). Gas (Y) treatment with Mg, produces a white solid substance.....

- (A)  $\text{Mg}_3\text{N}_2$  (B)  $\text{MgO}$   
 (C)  $\text{Mg}_2\text{O}_3$  (D)  $\text{MgCl}_2$

**Sol.**Q.6 Conc.  $\text{HNO}_3$  is yellow coloured liquid due to

- (A) dissolution of NO in conc.  $\text{HNO}_3$   
 (B) dissolution of  $\text{NO}_2$  in conc.  $\text{HNO}_3$   
 (C) dissolution of  $\text{N}_2\text{O}$  in conc.  $\text{HNO}_3$   
 (D) dissolution of  $\text{N}_2\text{O}_3$  in conc.  $\text{HNO}_3$

**Sol.**

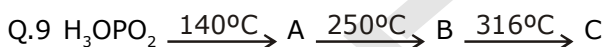
Q.7 A gas at low temperature does not react with the most of compounds. It is almost inert and is used to create intent atmosphere in bulbs. The combustion of this gas is exceptionally an endothermic reaction Based on the given information, we can conclude that the gas is.

- (A) oxygen (B) nitrogen  
 (C) carbon mono-oxide (D) hydrogen

**Sol.**

Q.8 when chlorine gas is passed through an aqueous solution of a potassium halide in the presence of chloroform a violet colouration is obtained. On passing more of chlorine water, the violet colour is disappeared and solution becomes colourless. This test confirms the presence of ..... in aqueous solution.

- (A) chlorine (B) fluorine  
(C) bromine (D) iodine

**Sol.**

Compound (C) is

- (A)  $\text{H}_2\text{PO}_3$  (B)  $\text{H}_3\text{PO}_3$   
(C)  $\text{HPO}_3$  (D)  $\text{H}_4\text{P}_2\text{O}_7$

**Sol.**

Q.10 An explosive compound (A) reacts with water to produce  $\text{NH}_4\text{OH}$  and  $\text{HOCl}$ . Then, the compound (A), is

- (A) TNG (B)  $\text{NCl}_3$   
(C)  $\text{PCl}_3$  (D)  $\text{HNO}_3$

**Sol.**

Q.11 An inorganic salt (A) is decomposed at about 523 K to give products (B) and (C). Compound (C) is a liquid at room temperature and is neutral to litmus paper while oxide (B) on burning with white phosphorous given a dehydrating agent (D). Compounds (A), (B), (C) and (D) will be identified as  $\text{N}_2\text{O}$ .

- (A)  $\text{NH}_4\text{NO}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{P}_2\text{O}_5$   
(B)  $\text{NH}_4\text{NO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{H}_2\text{O}$ ,  $\text{P}_2\text{O}_5$   
(C)  $\text{CaCO}_3$ ,  $\text{CaO}$ ,  $\text{H}_2\text{O}$ ,  $\text{CaCl}_2$   
(D)  $\text{CaCO}_3$ ,  $\text{CaO}$ ,  $\text{H}_2\text{O}$ ,  $\text{Ca}(\text{OH})_2$

**Sol.**

Q.12. An inorganic compound (A) made of two most occurring elements into the earth crust, having polymeric tetra-hedral net work structure. With carbon, compound (A) produces a poisonous gas (B) which is the most stable diatomic molecule. Compounds (A) and (B) will be

- (A)  $\text{SiO}_2$ ,  $\text{CO}_2$  (B)  $\text{SiO}_2$ ,  $\text{CO}$   
(C)  $\text{SiC}$ ,  $\text{CO}$  (D)  $\text{SiO}_2$ ,  $\text{N}_2$

**Sol.**

Q.13. A sulphate of a metal (A) on heating evolves two gases (B) and (C) and an oxide (D). Gas (B) turns  $\text{K}_2\text{Cr}_2\text{O}_7$  paper green while gas (C) forms a trimer in which there is non S-S bond. Compounds (D) with  $\text{HCl}$ , forms a Lewis base (E) which exists as a dimer. Compounds (A), (B), (C), (D) and (E) are respectively

- (A)  $\text{FeSO}_4$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCl}_3$   
(B)  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeCl}_3$   
(C)  $\text{FeS}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{FeSO}_4$ ,  $\text{FeCl}_3$   
(D)  $\text{FeS}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{Fe}_2(\text{PO}_4)_3$ ,  $\text{FeCl}_2$

**Sol.**

Q.14 A tetra atomic molecule (A) on reaction with nitrogen (I) oxide, produces two substances (B) and (C), (B) is a dehydrating agent in its monomeric form while substance (C) is a diatomic gas which shows almost inert behavior. The substances (A) and (B) and (C) respectively will be

- (A)  $P_4, P_4O_{10}, N_2$  (B)  $P_4, N_2O_5, N_2$   
 (C)  $P_4, P_2O_3, Ar$  (D)  $P_4, P_2O_3, H_2$

**Sol.**

Q.15 First compound of inert gases was prepared by scientist Neil Barthleta in 1962. This compound is

- (A)  $XePtF_6$  (B)  $XeO_3$   
 (C)  $XeF_6$  (D)  $XeOF_4$

**Sol.**

Q.16 Carbon give has X% of  $CO_2$  and is used as an antidote for poisoning of Y. Then, X and Y are

- (A) X = 95% and Y = lead poisoning  
 (B) X = 5% and Y = CO poisoning  
 (C) X = 30% and Y =  $CO_2$  poisoning  
 (D) X = 45% and Y = CO poisoning

**Sol.**

Q.17 The correct order of acidic strength of oxide of nitrogen is

- (A)  $NO < NO_2 < N_2O < N_2O_3 < N_2O_5$   
 (B)  $N_2O < NO < N_2O < N_2O_4 < N_2O_5$   
 (C)  $NO < N_2O < N_2O_3 < N_2O_5 < N_2O_4$   
 (D)  $NO < N_2O < N_2O_5 < N_2O_3 < N_2O_4$

**Sol.**

Q.18 Nitrogen dioxide is dissolved in water to produce

- (A)  $HNO_3$  and  $HNO_2$  (B) only  $HNO_3$   
 (C) only  $HNO_2$  (D)  $HNO_2$  and  $N_2$

**Sol.**

Q.19 Consider two reactions

- I.  $Zn + \text{conc. } HNO_3 (\text{hot}) \rightarrow Zn(NO_3)_2 + X + H_2O$   
 II.  $Zn + \text{dil. } HNO_3 (\text{cold}) \rightarrow Zn(NO_3)_2 + Y + H_2O$

Compounds X and Y are respectively

- (A)  $N_2O, NO$  (B)  $NO_2, N_2O$   
 (C)  $N_2, N_2O$  (D)  $NO_2, NO$

**Sol.**

Q.20  $H_3BO_3 \xrightarrow{T_1} X \xrightarrow{T_2} Y \xrightarrow{\text{red hot}} B_2O_3$

if  $T_1 < T_2$  then X and Y respectively are

- (A) X = Metaboric acid and Y = Tetraboric acid  
 (B) X = Tetraboric acid and Y = Metaboric acid  
 (C) X = Borax and Y = Metaboric acid  
 (D) X = Tetraboric acid and Y = Borax

**Sol.**

Q.21 Boron forms  $BX_3$  type of halides. The correct increasing order of Lewis - acid strength of these halides is

- (A)  $BF_3 > BCl_3 > BBr_3 > BI_3$   
 (B)  $BI_3 > BBr_3 > BCl_3 > BF_3$   
 (C)  $BF_3 > BI_3 > BCl_3 > BBr_3$   
 (D)  $BF_3 > BCl_3 > BI_3 > BBr_3$

Sol.

Q.22 Which one of the following compounds on strong heating evolves ammonia gas ?

- (A)  $(\text{NH}_4)_2\text{SO}_4$  (B)  $\text{HNO}_3$   
(C)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (D)  $\text{NH}_3\text{NO}_3$

Sol.

Q.23 The compound  $(\text{SiH}_3)_3\text{N}$  is

- (A) pyramidal and more basic than  $(\text{CH}_3)_3\text{N}$   
(B) planar and less basic than  $(\text{CH}_3)_3\text{N}$   
(C) pyramidal and less basic than  $(\text{CH}_3)_3\text{N}$   
(D) pyramidal and more basic than  $(\text{CH}_3)_3\text{N}$

Sol.

Q.24 The correct order of acid strength of oxyacids of chlorine is

- (A)  $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$   
(B)  $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$   
(C)  $\text{HClO} > \text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2$   
(D)  $\text{HClO}_4 < \text{HClO}_2 > \text{HClO}_3 > \text{HClO}$

Sol.

Q.25 In a molecule of phosphorus (V) oxide, there are

- (A) 4P-P, 10 P-O and 4P=O bonds  
(B) 12P-O, and 4P=O bonds  
(C) 2P-O and 4P=P bonds  
(D) 6P-P, 12P-O and 4P=P bonds

Sol.

Q.26 The structures of  $\text{O}_3$  and  $\text{N}_3^-$  are

- (A) linear and bent, respectively  
(B) both linear  
(C) both bent  
(D) bent and linear, respectively

Sol.

Q.27 When conc.  $\text{H}_2\text{SO}_4$  was treated with  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , CO gas was evolved. By mistake, somebody used dilute  $\text{H}_2\text{SO}_4$  instead of conc.  $\text{H}_2\text{SO}_4$  then the gas evolved was

- (A) CO (B) HCN  
(C)  $\text{N}_2$  (D)  $\text{CO}_2$

Sol.

Q.28 (A) +  $\text{O}_2 \longrightarrow \text{X} + \text{Y} + \text{Z}$   
(organic Compound)

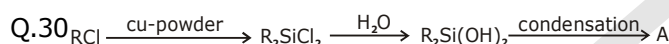
Compound (A) in pure form does not give ppt. with  $\text{AgNO}_3$  solution. A mixture containing 70% of (A) and 30% of ether is used as an anaesthetic. Compound (X) and (Y) are oxides while (Z) is a pungent smelling gas. (X) is a neutral oxide which turns cobalt chloride paper pink. Compound (Y) turns lime water milky and produces an acidic solution with water. Compounds (A), (X), (Y) and (Z) respectively will be

- (A)  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$   
(B)  $\text{CHCl}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$   
(C)  $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2$   
(D)  $\text{NH}_2\text{CONH}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$

**Sol.**

Q.29 An inorganic white crystalline compound (A) has a rock salt structure (A) on reaction with conc.  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$ , evolves a pungent smelling, greenish-yellow gas (B). Compound (A) gives white ppt. of (C) with  $\text{AgNO}_3$  solution. Compounds (A), (B) and (C) will be respectively

- (A)  $\text{NaCl}$ ,  $\text{Cl}_2$ ,  $\text{AgCl}$       (B)  $\text{NaBr}$ ,  $\text{Br}_2$ ,  $\text{NaBr}$   
 (C)  $\text{NaCl}$ ,  $\text{Cl}_2$ ,  $\text{Ag}_2\text{SO}_4$     (D)  $\text{Na}_2\text{CO}_3$ ,  $\text{CO}_2$ ,  $\text{Ag}_2\text{CO}_3$

**Sol.**

Compound (A) is

- (A) a linear silicone      (B) a chlorosilane  
 (C) a linear silone      (D) a network silone

**Sol.**

Q.31 When oxalic acid reacts with conc.  $\text{H}_2\text{SO}_4$ , two gases produced are of neutral and acidic in nature respectively. Potassium hydroxide absorbs one of the two gases. The product formed during this absorption and the gas which gets absorbed are respectively

- (A)  $\text{K}_2\text{CO}_3$  and  $\text{CO}_2$       (B)  $\text{KHCO}_3$  and  $\text{CO}_2$   
 (C)  $\text{K}_2\text{CO}_3$  and  $\text{CO}$       (D)  $\text{KHCO}_3$  and  $\text{CO}$

**Sol.**

Q.32 Concentrated  $\text{HNO}_3$  reacts with iodine to give

- (A)  $\text{HI}$       (B)  $\text{HOI}$   
 (C)  $\text{HOIO}_2$       (D)  $\text{HOIO}_3$

**Sol.**

Q.33 Conc.  $\text{H}_2\text{SO}_4$  cannot be used to prepare  $\text{HBr}$  from  $\text{NaBr}$  because it

- (A) reacts slowly with  $\text{NaBr}$   
 (B) oxidises  $\text{HBr}$   
 (C) reduces  $\text{HBr}$   
 (D) disproportionates  $\text{HBr}$

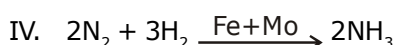
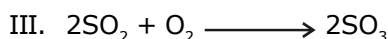
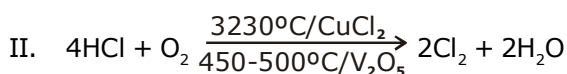
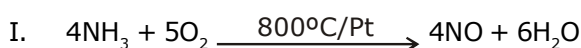
**Sol.**

Q.35 Molecular shapes of  $\text{SF}_4$ ,  $\text{CF}_4$  and  $\text{XeF}_4$  are

- (A) the same, with 2, 0 and 1 lone pairs of electrons respectively  
 (B) the same, with 2, 0 and 1 lone pairs of electrons respectively  
 (C) the different, with 0, 1 and 2 lone pairs of electrons respectively  
 (D) the different, with 1, 0 and 2 lone pairs of electrons respectively

**Sol.**

Q.36 Match List-I with List - II

**List-I Chemical reaction**



**List II Name of process**

- (a) Contact process  
 (b) Ostwald's process  
 (c) Deacon's process  
 (d) Haber's process  
 (A) I-a, II, b, III-d, IV, c  
 (B) I, b, II-c, III-a, IV-d  
 (C) I-a, II-d, III- c, IV-d  
 (D) I-a, II-c, III-b, IV -d

**Sol.**

Q.37 Ammonia can be dried by

- (A) conc.  $\text{H}_2\text{SO}_4$  (B)  $\text{P}_4\text{O}_{10}$   
 (C)  $\text{CaO}$  (D) anhydrous  $\text{CaCl}_2$

**Sol.**

Q.38 When chlorine reacts with a gas X, an explosive inorganic compound Y' is formed. Then X and Y will

- (A)  $\text{X} = \text{O}_2$  and  $\text{Y} = \text{NCl}_3$   
 (B)  $\text{X} = \text{NH}_3$  and  $\text{Y} = \text{NCl}_3$   
 (C)  $\text{X} = \text{O}_2$  and  $\text{Y} = \text{NH}_4\text{Cl}$   
 (D)  $\text{X} = \text{NH}_3$  and  $\text{Y} = \text{NH}_4\text{Cl}$

**Sol.**Q.39 The solubility of anhydrous  $\text{AlCl}_3$  and hydrous  $\text{AlCl}_3$  in diethyl ether are  $S_1$  and  $S_2$  respectively. Then

- (A)  $S_1 = S_2$  (B)  $S_1 > S_2$   
 (C)  $S_1 < S_2$  (D)  $S_1 < S_2$  but not  $S_1 = S_2$

**Sol.**

Q.40 Which one of the following statements is not true regarding diborane ?

- (A) It has two bridging hydrogens and four perpendicular to the rest  
 (B) When methylated, the product is  $\text{Me}_4\text{B}_2\text{H}_2$ .  
 (C) The bridging hydrogens are in a plane perpendicular to the rest  
 (D) All the B-H bond distances are equal

**Sol.**Q.41 When  $\text{AgNO}_3$  is heated strongly, the products formed are

- (A)  $\text{NO}$  and  $\text{NO}_2$  (B)  $\text{NO}_2$  and  $\text{O}_2$   
 (C)  $\text{NO}_2$  and  $\text{N}_2\text{O}$  (D)  $\text{NO}$  and  $\text{O}_2$

**Sol.**Q.42  $\text{HNO}_3 + \text{P}_4\text{O}_{10} \longrightarrow \text{HPO}_3 + \text{A}$ ; the product A is

- (A)  $\text{N}_2\text{O}$  (B)  $\text{N}_2\text{O}_3$   
 (C)  $\text{NO}_2$  (D)  $\text{N}_2\text{O}_5$

**Sol.**

Q.43 Which of the following is the correct order of acidic strength ?

- (A)  $\text{Cl}_2\text{O}_7 > \text{SO}_2 > \text{P}_4\text{O}_{10}$  (B)  $\text{CO}_2 > \text{N}_2\text{O}_5 > \text{SO}_3$   
 (C)  $\text{Na}_2\text{O} > \text{MgO} > \text{Al}_2\text{O}_3$  (D)  $\text{K}_2\text{O} > \text{CaO} > \text{MgO}$

**Sol.**

Compound (A) is used a/an

- (A) fertilizer (B) dehydrating agent  
(C) oxidising agent (D) reducing agent

**Sol.**

Q.45 A gas which exists in three allotropic forms  $\alpha$ ,  $\beta$  and  $\gamma$  is

- (A)  $\text{SO}_2$  (B)  $\text{SO}_3$   
(C)  $\text{CO}_2$  (D)  $\text{NH}_3$

**Sol.**

Q.46 A red coloured mixed oxide (X) on treatment with cone.  $\text{HNO}_3$  gives a compound (Y). (Y) with  $\text{HCl}$ , produces a chloride compound (Z) which can also be produced by treating (X) with cone.  $\text{HCl}$

Compound (X), (Y) and (Z) will be

- (A)  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}_2$ ,  $\text{MnCl}_2$  (B)  $\text{Pb}_3\text{O}_4$ ,  $\text{PbO}_2$ ,  $\text{PbCl}_2$   
(C)  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCl}_2$  (D)  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCl}_3$

**Sol.**

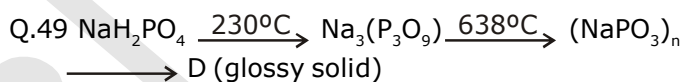
Q.47 There is no S-S bond in

- (A)  $\text{S}_2\text{O}_4^{2-}$  (B)  $\text{S}_2\text{O}_5^{2-}$   
(C)  $\text{S}_2\text{O}_3^{2-}$  (D)  $\text{S}_2\text{O}_7^{2-}$

**Sol.**

Q.48 One mole of calcium phosphide on reaction with excess of water gives

- (A) one mole of phosphine  
(B) two moles of phosphoric acid  
(C) two moles of phosphine  
(D) one mole of phosphorus penta-oxide

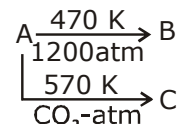
**Sol.**

Compound (D) is sodium hexametaphosphate which is known as

- (A) Bunsen's salt (B) Graham's salt  
(C) Reimann's salt (D) Werner's salt

**Sol.**

Q.50 Three allotropes (A), (B) and (C) of phosphorus in the following change are respectively



- (A) white, black, red (B) black, white, red  
(C) red, black, white (D) red, violet, black

**Sol.**

## EXERCISE – II

## OBJECTIVE PROBLEMS (JEE ADVANCED)

1. When an inorganic compound react with  $\text{SO}_2$  in aqueous medium, produces (A). (A) one reaction with  $\text{Na}_2\text{CO}_3$ , gives compound (B) which with sulphur, gives a substance (C) sued in pictography. Compound (C) is

- (A)  $\text{Na}_2\text{S}$  (B)  $\text{Na}_2\text{S}_2\text{O}_7$   
(C)  $\text{Na}_2\text{SO}_4$  (D)  $\text{Na}_2\text{S}_2\text{O}_3$

Sol.

2. Borax is actually made of two tetrahedra and two triangular units joined together and should be written as :  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$

Consider the following statement about borax :

- a. Each boron atom has four B–O bond  
b. Each boron atom has three B–O bonds  
c. Two boron atoms have four B–O bonds while other two have three B–O bonds  
d. Each boron atom has one –OH groups

Select correct statement(s) :

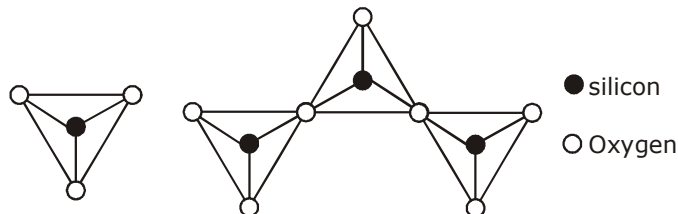
- (A) a, b (B) b, c  
(C) c, d (D) a, c

Sol.

**Question N. 3 to 5 (3 questions)**

Read name '**silica**' covers an entire group of minerals, which have the general formula  $\text{SiO}_2$ , the mole common of which is quartz. Quartz is form work silicane with  $\text{SiO}_4$  tetrahedra arranged in spirals. The spirals can turn in a clockwise or anticlockwise direction a feature that results in there being two mirror images, optically active, varieties of quartz.

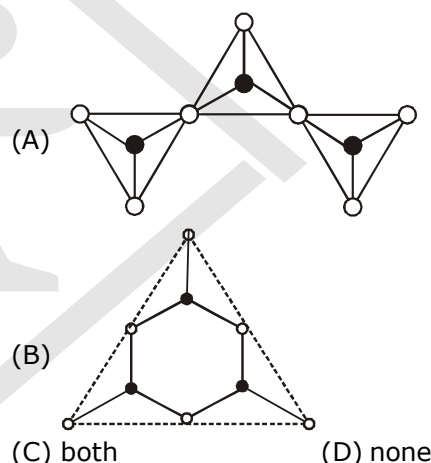
3. The following pictures represent various silicate anions. Their formulae are respectively



- (A)  $\text{SiO}_3^{2-}$   $\text{Si}_3\text{O}_7^{2-}$  (B)  $\text{SiO}_4^{4-}$   $\text{Si}_3\text{O}_{10}^{8-}$   
(C)  $\text{SiO}_4^{2-}$   $\text{Si}_3\text{O}_9^{2-}$  (D)  $\text{SiO}_3^{4-}$   $\text{Si}_3\text{O}_7^{8-}$

Sol.

4.  $\text{Si}_3\text{O}_9^{6-}$  (having three tetrahefral) is represented as :



Sol.

5. The silicate anion in the mineral kinotite is a Chian of three  $\text{SiO}_4$  tetrahedra that share corners with adjacent tetrahedra. The mineral also contains  $\text{Ca}^{2+}$  ions,  $\text{Cu}^{2+}$  ions and water molecule in a 1 : 1 : 1 ratio mineral is represented as "

- (A)  $\text{CaCuSi}_3\text{O}_{10} \cdot \text{H}_2\text{O}$  (B)  $\text{CaCuSi}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$   
(C)  $\text{Ca}_2\text{Cu}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$  (D) none of these

Sol.

**Question No. 6 to 7 (2 questions)**

Question given below are based on electronic configurations of the element. The three X, Y and Z with the electronic configurations shown below all form hydrides :

Element	Electronic configuration
X	$1s^2, 2s^2, 2p^3$
Y	$1s^2, 2s^2, 2p^6, 3s^1$
Z	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^5$

6. Which line of properties (A, B, C or D) correctly lists properties of the hydrides of these elements

	Hydride of X	Hydride of Y	Hydride of Z
(A)	Colourless gas insoluble in $H_2O$	Silver/grey solid, reacts with $H_2O$ to form an alkaline solution	Colourless gas from a strong acid in $H_2O$
(B)	Colourless liquid, no reaction with $H_2O$	Silver/grey solid, forms $H_2O$	Ionic solid with formula $ZH$
(C)	Colourless gas found naturally	Does not conduct electricity in the molten state	Colourless gas, reacts with $Cl_2$
(D)	Non-polar compound reaction with $Cl_2$ in light	Silver/grey ionic solid with formula $YH_2$	Forms when water is added to phosphorus and element Z

Sol.

7. Which of the following exists as gas ?  
 (A)  $X_2$  (B)  $Y_2$   
 (C)  $Z_2$  (D) all of the above

Sol.

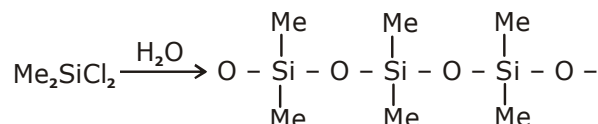
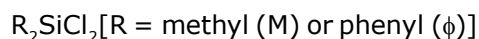
**Question No. 8 to 9 (2 questions)**

Read the following write-ups and answer the questions at the end of it.

Silicons are synthetic polymers containing represented  $R_2SiO$  units. Since, the empirical formula is that of aketone ( $R_2CO$ ) the same silicone has been given to these. Silicones can be made

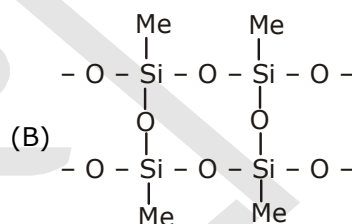
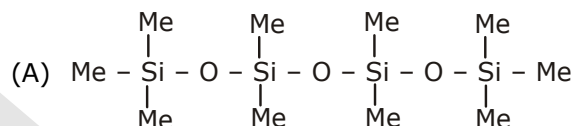
into oils, rubbery elastomers and resins. They find a variety of applications because of their chemical inertness, water repelling nature, heat-resistance and good electrical insulating property.

Commercial silicon polymers are usually methyl derivatives and to a lesser extent phenyl derivatives and are synthesised by the hydrolysis of



Sol.

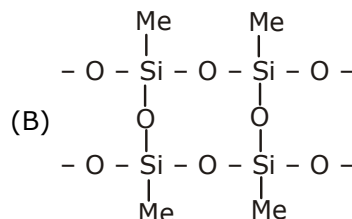
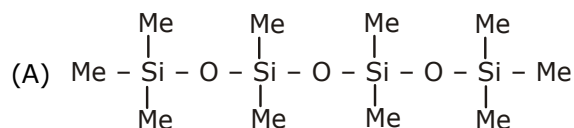
8. If we mix  $Me_3SiCl$  with  $Me_2SiCl_2$ , we get silicones of they type :



- (C) both of the above  
 (D) none of the above

Sol.

9. If we start with  $MeSiCl_3$  as the starting material, silicones formed is :



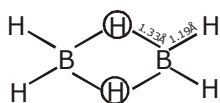
- (C) both of the above (D) none of the above

**Sol.**

10. The molecular shapes of diborane is shown :  
Consider the following statements for diborane :

1. Boron is approximately  $sp^3$  hybridised
2. B-H-B angle is  $180^\circ$
3. There are two terminal B-H bonds for each boron atom
4. There are only 12 bonding electrons available

Of these statements :

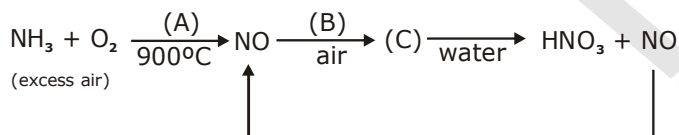


- (A) 1, 3 and 4 are correct  
(B) 1, 2 and 3 are correct  
(C) 2, 3 and 4 are correct  
(D) 1, 2 and 4 are correct

**Sol.**

### Question No. 11 to 12 (2 questions)

The following flow diagram represented the industrial preparation of nitric acid from ammonia



Answer the questions given below :

11. Which line of entry describes the undefined reagents, products and reaction conditions ?

A	B	C
(A) catalyst	R.T. ( $25^\circ\text{C}$ )	$\text{NO}_2$
(B) catalyst	R.T. ( $25^\circ\text{C}$ )	$\text{H}_2\text{O}$
(C) catalyst	high pressure	$\text{NO}_2$
(D) high pressure	catalyst	$\text{N}_2\text{O}_3$

**Sol.**

12. Formation of  $\text{HNO}_3$  when (C) is dissolved in  $\text{H}_2\text{O}$  takes place through various reactions. Select the reaction not observed in this step.

- (A)  $\text{NO}_2 + \text{H}_2\text{O} \longrightarrow \text{HNO}_3 + \text{HNO}_2$  (B)  $\text{HNO}_2 \longrightarrow \text{H}_2\text{O} + \text{NO} + \text{NO}_2$   
(C)  $\text{NO}_2 + \text{H}_2\text{O} \longrightarrow \text{HNO}_3 + \text{NO}$  (D) none of these

**Sol.**

13.  $\text{B(OH)}_3 + \text{NaOH} \rightleftharpoons \text{NaBO}_2 + \text{Na[B(OH)}_4] + \text{H}_2\text{O}$   
How can this reaction is made to proceed in forward direction ?

- (A) addition of cis 1,2 diol  
(B) addition of borax  
(C) addition of trans, 1, 2 diol  
(D) addition of  $\text{Na}_2\text{HPO}_4$

**Sol.**

14. **Assertion :** Borax bead test is applicable only to coloured salt.

**Reaction :** In borax bead test, coloured salts are decomposed to give coloured metal meta borates.

**Sol.**

15. **Assertion :** Aluminium and zinc metal evolve  $\text{H}_2$  gas from  $\text{NaOH}$  solution

**Reaction :** Several non-metals such as P, S, Cl, etc. yield a hydride instead of  $\text{H}_2$  gas from  $\text{NaOH}$

**Sol.**

16. **Assertion :** Conc.  $\text{H}_2\text{SO}_4$  can not be used to prepare pure  $\text{HBr}$  from  $\text{NaBr}$

**Reaction :** It react slowly with  $\text{NaBr}$ .

**Sol.**

17. **Assertion :** Oxygen is more electronegative than sulphur, yet  $\text{H}_2\text{S}$  is acidic, while  $\text{H}_2\text{O}$  is neutral.

**Reaction :** H – S bond is weaker than O–H bond.

**Sol.**

18. **Assertion :**  $\text{Al}(\text{OH})_3$  is amphoteric in nature.

**Reaction :** It can not be used as an antacid.

**Sol.**

19. **Assertion :** Chlorine gas disproportionate in hot & conc. NaOH solution.

**Reaction :** NaCl and NaOCl are formed in the above reaction.

**Sol.**

20. **Assertion :** Silicones are very inert polymers.

**Reaction :** Both Si – O and Si – C bond energies are very high.

**Sol.**

21. **Assertion :** Liquid  $\text{IF}_5$  conducts electricity.

**Reaction :** Liquid  $\text{IF}_5$  self ionizes are  $2\text{IF}_5 \rightleftharpoons \text{IF}_4^+ + \text{IF}_6^-$

**Sol.**

#### Paragraph of Question No. 22 to 24

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of  $\text{NH}_3$  and  $\text{PH}_3$ . Phosphine is a flammable gas and is prepared from white phosphorus.

22. Among the following, the correct statement is  
(A) Phosphates have no biological significance in humans  
(B) Between nitrates and phosphates, phosphates are less abundant in earth's crust  
(C) Between nitrates and phosphates, nitrates are less abundant in earth's crust  
(D) Oxidation of nitrates is possible in soil

**Sol.**

23. Among the following, the correct statement is :  
(A) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional  
(B) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional  
(C) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional  
(D) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional.

**Sol.**

24. White phosphorus on reaction with NaOH given  $\text{PH}_3$  as one of the products. This is a  
(A) dimerization reaction  
(B) disproportionation reaction  
(C) condensation reaction  
(D) precipitation reaction

**Sol.**

25. Which of the following is correct ?  
(A) The members of  $\text{B}_n\text{H}_{n+6}$  are less stable than  $\text{B}_n\text{H}_{n+4}$  series  
(B) Diborane is coloured and unstable at room temperature  
(C) The reaction of diborane with oxygen is endothermic  
(D) All of the above

**Sol.**

## p-Block Elements

26. In which of the following, a salt of the type  $KMO_2$  is obtained ?

- (A)  $B_2H_6 + KOH(aq.) \longrightarrow$   
 (B)  $Al + KOH(aq.) \longrightarrow$   
 (C) Both (D) None of these

**Sol.**

27. The general formula of cyclic or ring silicates is :

- (A)  $(Si_2O_5)_n^{2n-}$  (B)  $(SiO_3)_n^{2n-}$   
 (C)  $(SiO_3^{2-})_n$  (D) both (b) and (c)

**Sol.**

28. Silica reacts with magnesium to form a magnesium compound (X). (X) reacts with dilute HCl and forms (Y). (Y) is :

- (A)  $MgO$  (B)  $MgCl_2$   
 (C)  $MgSiO$  (D)  $SiCl_4$

**Sol.**

29. Silica is reacted with sodium carbonate. What is the gas liberated ?

- (A)  $CO$  (B)  $O_2$   
 (C)  $CO_2$  (D)  $O_3$

**Sol.**

30. Fire extinguishers contain a bottle of  $H_2SO_4$  and:

- (A)  $CaCO_3$  (B)  $MgCO_3$   
 (C)  $NaHCO_3$  (D) any carbonate

**Sol.**

31. Which one of the oxides of nitrogen dimerises into colourless solid/liquid on cooling ?

- (A)  $N_2O$  (B)  $NO$   
 (C)  $N_2O_3$  (D)  $NO_2$   
 (E)  $N_2O_5$

**Sol.**

32. Ammonia reacts with Nessler's reagent to give :

- (A) deep blue precipitate (B) white precipitate  
 (C) green precipitate (D) brown precipitate

**Sol.**

33. When  $NH_4OH$  is added to copper sulphate solution, blue colour is obtained due to formation of :

- (A)  $Cu(NH_3)_4SO_4$  (B)  $Cu(NH_4SO_4)_2$   
 (C)  $Cu(OH)_2$  (D)  $CuO$

**Sol.**

34. The reaction between  $\text{NH}_2^-$  and  $\text{N}_2\text{O}$  gives :

- (A) NO (B)  $\text{N}_2\text{O}_5$   
(C)  $\text{NH}_2\text{NH}_2$  (D)  $\text{N}_3^-$

**Sol.**

35. Which of the following is a cyclic oxoacid ?

- (A)  $\text{H}_4\text{P}_2\text{O}_7$  (B)  $\text{H}_4\text{P}_2\text{O}_6$   
(C)  $\text{H}_5\text{P}_5\text{O}_{15}$  (D)  $\text{H}_3\text{P}_3\text{O}_9$

**Sol.**

36. For  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_4$ , the correct choice is :

- (A)  $\text{H}_3\text{PO}_3$  is dibasic and reducing  
(B)  $\text{H}_3\text{PO}_3$  is dibasic and non-reducing  
(C)  $\text{H}_3\text{PO}_4$  is tribasic and reducing  
(D)  $\text{H}_3\text{PO}_3$  is tribasic and non-reducing

**Sol.**

37. Which one of the following statements is wrong?

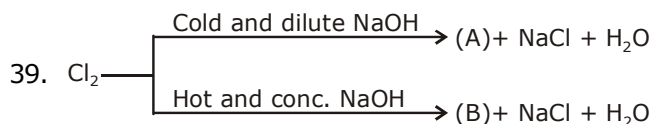
- (A)  $\text{H}_2\text{S}$  is a dibasic acid  
(B)  $\text{H}_2\text{S}$  acts only as a reducing agent  
(C) The bond angle in  $\text{H}_2\text{S}$  is  $109^\circ 28'$   
(D)  $\text{H}_2\text{S}$  has rotten smell

**Sol.**

38.  $\text{H}_2\text{S}$  is far more volatile than water because :

- (A) sulphur atom is more electronegative than oxygen atom  
(B) oxygen atom is more electronegative than sulphur atom  
(C)  $\text{H}_2\text{O}$  has bond angle of nearly  $105^\circ$   
(D) hydrogen atom is loosely bonded with sulphur

**Sol.**



Compounds (A) and (B) are :

- (A)  $\text{NaClO}_3$ ,  $\text{NaClO}$  (B)  $\text{NaOCl}_2$ ,  $\text{NaOCl}$   
(C)  $\text{NaClO}_4$ ,  $\text{NaClO}_3$  (D)  $\text{NaOCl}$ ,  $\text{NaClO}_3$

**Sol.**

40. When chlorine water is added to an aqueous solution of sodium halide in the presence of chloroform, a violet colouration is obtained. When more of chlorine water is added, the violet colour disappears and solution becomes colourless. This confirms that sodium halide is :

- (A) chloride (B) fluoride  
(C) bromide (D) iodide

**Sol.**

41. Which of the following oxyacids of chlorine is formed on shaking chlorine water with freshly precipitated yellow oxide of mercury ?

- (A)  $\text{HClO}_3$  (B)  $\text{HClO}_2$   
(C)  $\text{HClO}$  (D)  $\text{HClO}_4$

**Sol.**

42. Interhalogen compounds are more reactive than the individual halogen because :

- (A) two halogens are present in place of one  
(B) their bond energy is less than the bond energy of the halogen molecule  
(C) they are more ionic  
(D) they carry more energy



**Sol.**

43. Tincture iodine is :

- (A) aqueous solution of  $I_2$   
(B) solution of iodine in aqueous KI  
(C) alcoholic solution of  $I_2$   
(D) aqueous solution of KI

**Sol.**44. When  $F_2$  reacts with hot and conc. alkali, then following will be obtained :

- (i)  $OF_2$  (ii)  $O_2$  (iii)  $H_2O$  (iv)  $NaF$   
(A) (i), (iii) and (iv) (B) (ii) and (iii) only  
(C) (ii), (iii) and (iv) (D) all of these

**Sol.**

45. The following statements pertain to noble gases.

- (i) Argon is the most abundant (percentage 1% by volume) noble gas in the atmospheric air.  
(ii) Helium is the lightest non-inflammable gas.  
(iii) The valency of noble gases is zero.  
(iv) All noble gases are adsorbed by coconut charcoal.

The correct statements are :

- (A) (i), (ii) and (iii) (B) (ii) and (iv)  
(C) (iii) and (iv) (D) (ii), (iii) and (iv)

**Sol.**

46. The ease of liquefaction of noble gases is in the order :

- (A)  $Ne < He < Xe < Kr < Ar$   
(B)  $He < Ne < Ar < Kr < Xe$   
(C)  $Xe < Kr < Ar < Ne < He$   
(D)  $Ar < He < Xe < Kr < Ne$

**Sol.**

47. Which of the following does not react with fluorine ?

- (A) Kr (B) Xe (C) Ar (D) all of these

**Sol.**

48. Helium is added to oxygen used by deep seadivers because :

- (A) it is less soluble in blood than nitrogen under high pressure  
(B) it is lighter than nitrogen  
(C) it is readily miscible with oxygen  
(D) it is less poisonous than nitrogen

**Sol.**

49. Which of the following statements is not correct ?

- (A) Argon is used in electric bulbs  
(B) Krypton is obtained during radioactive disintegration  
(C) Half life of radon is only 3.8 days  
(D) Helium is used in producing very low temperatures

**Sol.**

50. Which of the following is used to attain very low temperature during cryoscopic studies?

- (A) Ar (B) He (C) Ne (D) Kr

**Sol.**

**EXERCISE – III****OBJECTIVE PROBLEMS (JEE ADVANCED)**

Q.1 Which of the following oxides are basic ?

- (A)  $B_2O_3$  (B)  $Tl_2O$   
(C)  $In_2O_3$  (D)  $Al_2O_3$

**Sol.**

Q.2 Stability of monovalent and trivalent cations of Ga, In, lie in following sequence :

- (A)  $Ga^{3+} < In^{3+} > Tl^{3+}$  (B)  $Ga^{3+} > In^{3+} > Tl^{3+}$   
(C)  $Tl^+ > In^+ > Ga^+$  (D)  $Ga^{3+} > In^+ > Tl^+$

**Sol.**

Q.3 Which of the following elements do not form carbide ?

- (A) B (B) Al (C) In (D) Ga

**Sol.**

Q.4 Orthoboric acid ( $H_3BO_3$ ) and metaboric acid ( $HBO_2$ ) differ in respect of :

- (A) basicity (B) structure  
(C) melting point (D) oxidation

**Sol.**

Q.5 Which of the given si/are amphoteric ?

- (A) BeO (B)  $Ag_2O$   
(C)  $CO_2$  (D)  $SnO_2$

**Sol.**

Q.6 Decomposition of oxalic acid in presence of conc.  $H_2SO_4$  gives :

- (A) CO (B)  $CO_2$   
(C) formic acid (D)  $H_2O$

**Sol.**

Q.7 Which of the following are true about silicones ?

- (A) They are formed by hydrolysis of  $R_2SiCl_2$   
(B) They are polymer, made up of  $R_2SiO_2$  units  
(C) They are made up of  $SiO_4^{4-}$  units  
(D) They are macromolecules

**Sol.**

Q.8 Which among the following statements are correct ?

- (A) Aqua dag and oil dag are made up of graphite
- (B) Graphite reacts with conc.  $\text{HNO}_3$  to form metallic acid  $\text{C}_6(\text{COOH})_6$
- (C)  $\text{C}_3\text{O}_2$  is also toxic like CO
- (D) Zircon,  $\text{ZrSiO}_4$  is a gemstone

**Sol.**

Q.9 The metals which produce hydrogen only with very dilute nitric acid are :

- (A) Zn    (B) Sn    (C) Mg    (D) Mn

**Sol.**

Q.10 Which of the following form oxychlorides as precipitate on hydrolysis ?

- (A)  $\text{BiCl}_3$                       (B)  $\text{SbCl}_3$
- (C)  $\text{CCl}_4$                       (D)  $\text{PbCl}_2$

**Sol.**

Q.11 Which of the following reactions can evolve phosphine ?

- (A) White P +  $\text{Ca}(\text{OH})_2 \longrightarrow$
- (B)  $\text{AlP} + \text{H}_2\text{O} \longrightarrow$
- (C)  $\text{H}_3\text{PO}_4 \xrightarrow{\text{Heat}}$
- (D)  $\text{PH}_4\text{I} + \text{NaOH} \longrightarrow$

**Sol.**

Q.12 Ammonia cannot be dried by :

- (A)  $\text{H}_2\text{SO}_4$                       (B)  $\text{P}_2\text{O}_5$
- (C)  $\text{CaO}(\text{anhyd.})$               (D)  $\text{CuSO}_4$

**Sol.**

Q.13 Which reagent does not give oxygen as one of the product during oxidation with ozone?

- (A)  $\text{SO}_2$                       (B)  $\text{SnCl}_2/\text{HCl}$
- (C)  $\text{H}_2\text{S}$                       (D)  $\text{PbS}$

**Sol.**

Q.14 Which of the elements show allotropy ?

- (A) N                              (B) P
- (C) As                              (D) Bi

**Sol.**

Q.15 Peroxoacids of sulphur are:

- (A)  $\text{H}_2\text{SO}_4$                       (B)  $\text{H}_2\text{SO}_3$
- (C)  $\text{H}_2\text{SO}_5$                       (D)  $\text{H}_2\text{S}_2\text{O}_8$

**Sol.**

Q.16 Identify the false statement?

- (A) Monoclinic sulphur is stable at room temperature  
 (B) Rhombic sulphur is stable at room temperature  
 (C) Both monoclinic and rhombic sulphur are soluble in  $\text{CS}_2$   
 (D) Rhombic sulphur is converted into monoclinic form but the reverse is not possible

**Sol.**

Q.17 HI can be prepared by which of the following methods?

- (A)  $\text{I}_2 + \text{H}_2\text{S}$  (B)  $\text{PI}_3 + \text{H}_2\text{O}$   
 (C)  $\text{KI} + \text{Conc. H}_2\text{SO}_4$   
 (D)  $\text{H}_2 + \text{I}_2$  in presence of Pt.

**Sol.**

Q.18 Select the correct statements?

- (A)  $\text{Cl}_2\text{O}$  and  $\text{ClO}_2$  are used as bleaching agents and germicides.  
 (B)  $\text{ClO}_2$  is the anhydride of  $\text{HClO}_2$  and  $\text{HClO}_3$   
 (C)  $\text{I}_2\text{O}_5$  is used in the quantitative estimation of CO  
 (D)  $\text{Cl}_2\text{O}_7$  is anhydride of  $\text{HClO}_3$

**Sol.**Q.19 Which of the following halide ions are oxidised by  $\text{MnO}_2$ ?

- (A)  $\text{Cl}^-$  (B)  $\text{Br}^-$   
 (C)  $\text{F}^-$  (D)  $\text{I}^-$

**Sol.**

Q.20 Which of the following are pseudohalide ions ?

- (A)  $\text{SCN}^-$  (B)  $\text{OCN}^-$   
 (C)  $\text{CN}^-$  (D)  $\text{ICl}_2^-$

**Sol.**

Q.21 What are the products formed in the reaction of xenon hexafluoride with silica?

- (A)  $\text{SeSiO}_4 + \text{HF}$  (B)  $\text{XeF}_2 + \text{SiF}_4$   
 (C)  $\text{SeOF}_4 + \text{SiF}_4$  (D)  $\text{XeO}_3 + \text{SiF}_4$

**Sol.**

Q.22 Which of the following two are isostructural ?

- (A)  $\text{XeF}_2$ ,  $\text{IF}_2^-$  (B)  $\text{NH}_3$ ,  $\text{BF}_3$   
 (C)  $\text{CO}_3^{2-}$ ,  $\text{SO}_3^{2-}$  (D)  $\text{PCl}_5$ ,  $\text{ICl}_5$

**Sol.**

Q.23  $\text{XeF}_6$  on hydrolysis gives:

- (A)  $\text{XeOF}_4$  (B)  $\text{XeO}_2\text{F}_2$   
(C)  $\text{XeO}_3$  (D)  $\text{XeO}_4$

**Sol.**

Q.24 Which among the following statements is/are correct?

- (A)  $\text{XeF}_4$  and  $\text{SbF}_5$  combine to form salt.  
(B) He and Ne do not form clathrates.  
(C) He has lowest b.pt. in its group.  
(D) He diffuses through rubber and polyvinyl chloride.

**Sol.**

### Passage-1

Aluminium is stable in air and water inspite of the fact that it is reactive metal. The reason is that a thin film of its oxide is formed on its surface which makes it passive for further attack. The layer is so useful that in industry, it is purposely deposited by an electrolytic process called anodising. Reaction of aluminium with oxygen is highly exothermic and is called thermite reaction.



Thermite reaction finds applications in the metallurgical attraction of many metals from their oxides and for welding of metals. The drawback is that to start the reaction, high temperature is required for which an ignition mixture is used.

Q.25 Anodising can be done by electrolysis of dilute  $\text{H}_2\text{SO}_4$  with aluminium as anode. This results in :

- (A) The formation of  $\text{Al}_2(\text{SO}_4)_3$  on the surface of aluminium anode  
(B) The formation of oxide film ( $\text{Al}_2\text{O}_3$ ) on the surface of aluminium anode  
(C) The formation of polymeric aluminium hydride film on the surface of aluminium anode  
(D) None of the above

**Sol.**

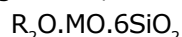
Q.26 The reaction which is not involved in thermite process:

- (A)  $3\text{Mn}_2\text{O}_3 + 8\text{Al} \rightarrow 9\text{Mn} + 4\text{Al}_2\text{O}_3$   
(B)  $\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{Cr} + \text{Al}_2\text{O}_3$   
(C)  $2\text{Fe} + \text{Al}_2\text{O}_3 \rightarrow \text{Fe}_2\text{O}_3 + 2\text{Al}$   
(D)  $\text{B}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{B} + \text{Al}_2\text{O}_3$

**Sol.**

### Passage-1

When a mixture of sodium carbonate and calcium carbonate is fused with silica at  $1500^\circ\text{C}$ , a liquid consisting silicates of sodium and calcium is formed. When this liquid is cooled, it becomes viscous and eventually ceases to flow. It becomes solid and called glass. By varying the proportions of the three basic ingredients and by adding other substances, the properties of glass can be altered. An approximate formula for ordinary glass may be given as,



Where  $\text{R} = \text{Na}$  or  $\text{K}$  and  $\text{M} = \text{Ca}$ ,  $\text{Ba}$ ,  $\text{Zn}$  and  $\text{Pb}$ .

$\text{SiO}_2$  may be replaced by  $\text{Al}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ .

Coloured glasses are obtained by adding certain metallic oxides or salts in the fused mass. Glass is attacked by  $\text{HF}$  and this property is used to make marking on the glass. This is known as etching.

The glass if cooled rapidly becomes brittle and fragile. The articles of glass are cooled neither very slowly nor very rapidly. The articles are cooled gradually. This process is termed annealing.

Q.27 Annealing is the best described as:

- (A) Slow and gradual cooling  
(B) Sudden and rapid cooling  
(C) Cooling by water  
(D) Very slow cooling

Sol.

Q.28 A blue colour can be imparted to glass by use of :

- (A)  $\text{Fe}_2\text{O}_3$  (B)  $\text{CoO}$   
(C)  $\text{NiO}$  (D)  $\text{Cu}_2\text{O}$

Sol.

Q.29 A special type of glass which contains cerium oxide and does not allow the passage of ultraviolet rays. This glass is used for making lenses. The glass is called:

- (A) Flint glass (B) Crooke's glass  
(C) hard glass (D) Pyrex glass

Sol.

**Passage-2**

The binary compounds of oxygen with other elements are called oxides. They are classified either depending upon their acid-base characteristics or on the basis of oxygen content.

**(a) Normal oxides :** These oxides which contain oxygen atoms as permitted by the normal oxidation number, i.e., -2. Normal oxide may be acidic, basic, amphoteric or neutral.

**(b) Polyoxides :** The oxides which contain oxygen atoms different than those permitted by the normal oxidation number of -2.

**(i) Peroxides :** Two oxygen atoms are linked to each other and each oxygen has -1 oxidation number. They contain (O – O) unit.

**(ii) Superoxides :** These oxides contain (O – O) $^{-1}$  unit. i.e., each O-atom has oxidation number – 1/2.

Q.30 Which pair of species is referred to as suboxides

- (A)  $\text{CO}$ ,  $\text{NO}$  (B)  $\text{SO}_2$ ,  $\text{CaO}$   
(C)  $\text{N}_2\text{O}$ ,  $\text{CO}$  (D)  $\text{N}_2\text{O}$ ,  $\text{C}_3\text{O}_2$

Sol.

Q.31 Which of the following pairs contains neutral oxides

- (A)  $\text{SO}_2$ ,  $\text{SO}_3$  (B)  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_5$   
(C)  $\text{CO}$ ,  $\text{NO}$  (D)  $\text{Na}_2\text{O}$ ,  $\text{CaO}$

Sol.

Q.32 Which of the following pairs contains mixed oxides

- (A)  $\text{Pb}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$  (B)  $\text{MnO}_2$ ,  $\text{BaO}_2$   
(C)  $\text{KO}_2$ ,  $\text{Na}_2\text{O}_2$  (D)  $\text{Mn}_3\text{O}_4$ ,  $\text{N}_2\text{O}_5$

Sol.

Q.33 Which of the following pairs contains amphoteric oxides

- (A)  $\text{BeO}$ ,  $\text{BaO}$  (B)  $\text{BeO}$ ,  $\text{Al}_2\text{O}_3$   
(C)  $\text{Al}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$  (D)  $\text{FeO}$ ,  $\text{CuO}$

Sol.

**Passage-3**

Halogens react with each other to form a number of compounds called inter halogen compounds. Their general formula is  $\text{AX}_n$ ; where A is less electronegative halogen while X is a more electronegative halogen and n is its number. The inter halogen compounds are essentially covalent and more reactive than the halogens since the bond A–X is weaker than A–A or X–X bond. The reactions of interhalogens are similar to those of halogens.

Q.34 Which of the following inter halogen compounds is not possible ?

- (A)  $\text{IF}_7$  (B)  $\text{IF}_5$   
(C)  $\text{ClF}_3$  (D)  $\text{FCl}_3$

Sol.

Q.35 Which halogen shows maximum oxidation state in forming inter halogen compound ?

- (A) I (B) Br  
(C) Cl (D) F

Sol.

Q.36 How many lone pairs of electrons are present on chlorine in  $\text{ClF}_3$  molecule ?

- (A) 0 (B) 1  
(C) 2 (D) 3

Sol.

Q.37 Which of the following statements is wrong for inter halogen ?

- (A) The value of  $n$  in  $\text{AX}_n$  (inter halogen) can be 1, 3, 5 or 7  
(B) The value of  $n$  in  $\text{AX}_n$  (inter halogen) can be 2, 4, or 6  
(C) A can never be fluorine as it is most electronegative halogen  
(D) X can never be iodine as it is least electronegative halogen.

Sol.

### Match the Column

#### 38. Match the Column

##### Column-I

- (A) Colemanite  
(B) Cryolite  
(C) Bauxite  
(D) Borax  
(E) Potash alum

##### Column-II

- (P)  $\text{Na}_3\text{AlF}_6$   
(Q)  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$   
(R)  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$   
(S)  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$   
(T)  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$

Sol.

#### 39. Match the Column

##### Column-I

- (A)  $\text{Cu} + \text{dil. HNO}_3$   
(B)  $\text{Cu} + \text{conc. HNO}_3$   
(C)  $\text{Zn} + \text{dil. HNO}_3$   
(D)  $\text{Zn} + \text{conc. HNO}_3$

##### Column-II

- (P) NO  
(Q)  $\text{NO}_2$   
(R)  $\text{N}_2\text{O}$   
(S)  $\text{Cu}(\text{NO}_3)_2$   
(T)  $\text{Cu}(\text{NO}_3)_2$

Sol.

#### 40. Match the Column

##### Column-I

- (A) Sulphur dioxide  
(B) Oxygen  
(C) Ozone  
(D) Hydrogen sulphide  
(E) Sulphur  
(F) Sulphuric acid  
(G) Fuming sulphuric acid  
(H) Peroxy disulphuric acid

##### Column-II

- (P) Laboratory reagent for mixture analysis  
(Q) Oleum  
(R) Vulcanizing rubber  
(S) Petroleum refining  
(T) Paramagnetic  
(U) Marshall's acid  
(V) Antichlor  
(W) Detection of double bond in organic compounds.

Sol.

#### 41. Match the Column

##### Column-I

- (A) Helium  
(B) Neon  
(C) Argon  
(D) Krypton  
(E) Xenon  
(F) Radon

##### Column-II

- (P) Lazy  
(Q) Hidden one  
(R) Stranger  
(S)  $1s^2, 2s^2, 2p^6$   
(T) Sun's element  
(U) Radioactive

Sol.

**Assertion Reason**

**42. Statement-1 :**  $\text{BF}_3$  is a weaker Lewis acid than  $\text{BCl}_3$

**Statement-2 :**  $\text{BF}_3$  molecule is stabilized to a greater extent than  $\text{BCl}_3$  by B-F  $\pi$ -bonding

**Sol.**

**43. Statement-1 :** Silicones are hydrophobic in nature.

**Statement-2 :** Si-O-Si linkages are moisture sensitive.

**Sol.**

**44. Statement-1 :**  $\text{H}_3\text{PO}_3$  and are tribasic acids as they contain three hydrogen atoms each.

**Statement-2 :** Both  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_4$  are reducing in nature.

**Sol.**

**45. Statement-1 :**  $\text{H}_2\text{SO}_4$  forms only one series of salts.

**Statement-2 :** The molecule of  $\text{H}_2\text{SO}_4$  consists of only one OH group.

**Sol.**

**46. Statement-1 :** All the halogens are coloured.

**Statement-2 :** Halogen molecules absorb some wavelengths of visible light and the electrons are promoted to higher energy molecular orbitals.

**Sol.**

**47. Statement-1 :** Helium and neon do not form clathrates.

**Statement-2 :** Both have smallest atomic size among all the elements of group 18.

**Sol.**

**48. Statement-1 :**  $\text{HClO}_4$  is a stronger acid than  $\text{HClO}_3$ .

**Statement-2 :** Oxidation state of chlorine in  $\text{HClO}_4$  is + 7 and in  $\text{HClO}_3$  it is +5.

**Sol.**

**49. Statement-1 :** Iodine displaces chlorine from  $\text{KClO}_3$ .

**Statement-2 :** Iodine is stronger oxidising agent than chlorine.

**Sol.**

**50. Statement-1 :** Fluorine does not show oxidation number greater than zero.

**Statement-2 :** The halogens chlorine, bromine and iodine can show positive oxidation states of +1, +3, +5 and +7.

**Sol.**



## EXERCISE – IV

## PREVIOUS YEARS

## LEVEL – I

## JEE MAIN

**Q.1** The correct no. of lone pairs on the central atom of compounds  $\text{XeF}_2$ ,  $\text{XeF}_4$  &  $\text{XeF}_6$  are respectively- **[AIEEE-2002]**

- (A) 3, 2, 1 (B) 4, 3, 2  
(C) 1, 3, 4 (D) 1, 2, 3

**Sol.**

**Q.2** The no. of  $\sigma$  bonds in the compound  $\text{P}_4\text{O}_{10}$  is - **[AIEEE-2002]**

- (A) 1 (B) 4  
(C) 3 (D) 16

**Sol.**

**Q.3** The number of hydrogen atoms (s) attached to phosphorus atom in hypophosphorous acid is - **[AIEEE-2005]**

- (A) two (B) zero  
(C) three (D) one

**Sol.**

**Q.4** What products are expected from the disproportionation reaction of hypochlorous acid - **[AIEEE-2006]**

- (A)  $\text{HClO}_2$  and  $\text{HClO}_4$  (B)  $\text{HCl}$  and  $\text{Cl}_2\text{O}$   
(C)  $\text{HCl}$  and  $\text{HClO}_3$  (D)  $\text{HClO}_3$  and  $\text{Cl}_2\text{O}$

**Sol.**

**Q.5** Which one of the following statements regarding helium is incorrect - **[AIEEE-2007]**

- (A) It is used to produce and sustain powerful superconducting magnets  
(B) It is used as a cryogenic agent for carrying out experiments at low temperatures  
(C) It is used to fill gas balloons instead of hydrogen because it is lighter than hydrogen and non-inflammable  
(D) It is used in gas-cooled nuclear reactors

**Sol.**

**Q.6** Which one of the following reactions of Xenon compounds is not feasible? **[AIEEE-2009]**

- (A)  $3 \text{XeF}_4 + 6 \text{H}_2\text{O} \rightarrow 2 \text{Xe} + \text{XeO}_3 + 12 \text{HF} + 1.5 \text{O}_2$   
(B)  $2 \text{XeF}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{Xe} + 4 \text{HF} + \text{O}_2$   
(C)  $\text{XeF}_6 + \text{RbF} \rightarrow \text{Rb}[\text{XeF}_7]$   
(D)  $\text{XeO}_3 + 6 \text{HF} \rightarrow \text{XeF}_6 + 3 \text{H}_2\text{O}$

**Sol.**

**Q.7** In which of the following arrangements, the sequence is not strictly according to the property written against it? **[AIEEE-2009]**

- (A)  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$  : increasing acid strength  
(B)  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$  : increasing basic strength  
(C)  $\text{B} < \text{C} < \text{O} < \text{N}$  : increasing first ionization enthalpy  
(D)  $\text{CO}_2 < \text{SiO}_2 < \text{SnO}_2 < \text{PbO}_2$  : increasing oxidising power

**Sol.**

**Q.8** Identify the incorrect statement from the following - **[AIEEE-2011]**

- (A) Ozone absorbs the intense ultraviolet radiation of the sun  
(B) Depletion of ozone layer is because of its chemical reactions with chlorofluoro alkanes  
(C) Ozone absorbs infrared radiation  
(D) Oxides of nitrogen in the atmosphere can cause the depletion of ozone layer

**Sol.**

**Q.9** The number of types of bonds between two carbon atoms in calcium carbide is - **[AIEEE-2011]**

- (A) One sigma, one pi  
(B) Two sigma, one pi  
(C) Two sigma, two pi  
(D) One sigma, two pi

**Sol.**

## LEVEL – II

## JEE ADVANCED

- Q.1** Nitrogen (I) oxide is produced by - [IIT-1989]  
 (A) Thermal decomposition of ammonium nitrate  
 (B) Disproportionation of  $\text{N}_2\text{O}_4$   
 (C) Thermal decomposition of ammonium nitrite  
 (D) Interaction of hydroxylamine and nitrous acid

Sol.

- Q.2** Nitrogen is liberated by the thermal decomposition of - [IIT-1991]  
 (A)  $\text{NH}_4\text{NO}_2$  (B)  $\text{NaN}_3$   
 (C)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (D) All the three

Sol.

- Q.3** There is no S – S bond in - [IIT-1991]  
 (A)  $\text{S}_2\text{O}_4^{2-}$  (B)  $\text{S}_2\text{O}_5^{2-}$   
 (C)  $\text{S}_2\text{O}_3^{2-}$  (D)  $\text{S}_2\text{O}_7^{2-}$

Sol.

- Q.4** The type of hybrid orbitals used by chlorine atom in  $\text{ClO}_2^-$  ion. [IIT-1992]  
 (A)  $\text{sp}^3$  (B)  $\text{sp}^2$   
 (C)  $\text{sp}$  (D) None

Sol.

## STATEMENT TYPE QUESTIONS :-

**Q.5 STATEMENT-I**

Although  $\text{PF}_5$ ,  $\text{PCl}_5$  and  $\text{PBr}_5$  are known, the pentahalides of nitrogen have not been observed

**STATEMENT-II**

Phosphorus has lower electronegativity than nitrogen. [IIT-1994]

- (A) Both statement-I and statement-II are true, and statement-II is the correct explanation of statement-I.  
 (B) Both statement-I and statement-II are true, but statement-II is not the correct explanation of statement-I  
 (C) statement-I is true but statement-II is false  
 (D) statement-I is false but statement-II is true.

Sol.

- Q.6** In  $\text{P}_4\text{O}_{10}$  each P atom is linked with.....O atoms -  
 (A) 2 (B) 3  
 (C) 4 (D) 5

Sol.

- Q.7** Which one of the following species is not a pseudohalide ?  
 (A)  $\text{CNO}^-$  (B)  $\text{RCOO}^-$   
 (C)  $\text{OCN}^-$  (D)  $\text{NNN}^-$

Sol.

- Q.8** Which of the following statements is correct for  $\text{CsBr}_3$  ? [IIT-1996]  
 (A) It is a covalent compound  
 (B) It contains  $\text{Cs}^{3+}$  and  $\text{Br}^-$  ions  
 (C) It contains  $\text{Cs}^+$  and  $\text{Br}_3^-$  ions  
 (D) It contains  $\text{Cs}^+$  and  $\text{Br}^-$  and lattice  $\text{Br}_2$  molecule

Sol.

- Q.9** Hydrolysis of one mole of peroxodisulphuric acid produces— **[IIT-1996]**  
(A) Two moles of sulphuric acid  
(B) Two moles of peroxomonosulphuric acid  
(C) One mole of sulphuric acid and one mole of peroxomonosulphuric acid  
(D) One mole each of sulphuric acid, peroxomonosulphuric acid and hydrogen peroxide.

**Sol.**

- Q.10** KF combines with HF to form  $\text{KHF}_2$ . The compound contains the species : **[IIT-1996]**  
(A)  $\text{K}^+$ ,  $\text{F}^-$  and  $\text{H}^+$  (B)  $\text{K}^+$ ,  $\text{F}^-$  and HF  
(C)  $\text{K}^+$  and  $[\text{HF}_2]^-$  (D)  $[\text{KHF}]^+$  and  $\text{F}^-$

**Sol.**

- Q.11** White phosphorus ( $\text{P}_4$ ) has - **[IIT-1998]**  
(A) Six P – P single bonds  
(B) Four P – P single bonds  
(C) two lone pairs of electrons  
(D) PPP angle of  $30^\circ$

**Sol.**

- Q.12** In Compound of type  $\text{ECl}_3$ , where E = B, P As or Bi, the angles Cl – E – Cl for different E are in the order **[IIT-1999]**  
(A)  $\text{B} > \text{P} = \text{As} = \text{Bi}$  (B)  $\text{B} > \text{P} > \text{As} > \text{Bi}$   
(C)  $\text{B} < \text{P} = \text{As} = \text{Bi}$  (D)  $\text{B} < \text{P} < \text{As} < \text{Bi}$

**Sol.**

- Q.13** On heating ammonium dichromate, the gas evolved is **[IIT-1999]**  
(A) oxygen (B) ammonia  
(C) nitrous oxide (D) nitrogen

**Sol.**

- Q.14** One mole of calcium phosphide on reaction with excess of water gives- **[IIT-1999]**  
(A) One mole of phosphine  
(B) Two moles of phosphoric acid  
(C) Two moles of phosphine  
(D) One mole of phosphorus oxide.

**Sol.**

- Q.15** The oxidation numbers of sulphur in  $\text{S}_8$ ,  $\text{S}_2\text{F}_2$ ,  $\text{H}_2\text{S}$ , respectively, are - **[IIT-1999]**  
(A) 0, + 1 and - 2 (B) + 2, + 1 and - 2  
(C) 0, + 1 and + 2 (D) - 2, + 1 and - 2

**Sol.**

- Q. 16** Ammonia can be dried by - **[IIT-2000]**  
(A) Conc.  $\text{H}_2\text{SO}_4$  (B)  $\text{P}_4\text{O}_{10}$   
(C) CaO (D) Anhydrous  $\text{CaCl}_2$

**Sol.**

- Q. 17** The number of P – O – P bonds in cyclic metaphosphoric acid is - **[IIT-2000]**  
(A) Zero (B) Two  
(C) Three (D) Four

**Sol.**

- Q.18** Amongst  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$ , the one with the highest boiling point is **[IIT-2000]**  
(A)  $\text{H}_2\text{O}$  because of hydrogen bonding  
(B)  $\text{H}_2\text{Te}$  because of higher molecular weight  
(C)  $\text{H}_2\text{S}$  because of hydrogen bonding  
(D)  $\text{H}_2\text{Se}$  because of lower molecular weight

- Q.19** The number of S – S bonds in sulphur trioxide trimer ( $S_3O_9$ ) is – **[IIT- 2001]**  
 (A) Three (B) Two  
 (C) One (D) Zero

**Sol.**

- Q.20** Read the following statement and explanation and answer as per the option given below :

**[IIT-2001]**

**Statement-I** : F atom has a less negative electron gain enthalpy affinity than Cl atom.

**Statement-II** : Additional electrons are repelled more effectively by 3 p electrons in Cl atom than by 2p electron in F atom

(A) If both Statement-I and Statement-II are correct, and Statement-II is the correct explanation of the Statement-I

(B) If both Statement-I and Statement-II are correct, but Statement-II is not correct explanation of the Statement-I

(C) If Statement-I is correct but Statement-II is incorrect

(D) If Statement-I is incorrect but Statement-II is correct

**Sol.**

- Q.21** The set with correct order of acidity is **[IIT- 2001]**

- (A)  $HClO < HClO_2 < HClO_3 < HClO_4$   
 (B)  $HClO_4 < HClO_3 < HClO_2 < HClO$   
 (C)  $HClO < HClO_4 < HClO_3 < HClO_2$   
 (D)  $HClO_4 < HClO_2 < HClO_3 < HClO$

**Sol.**

- Q.22** The reaction  $3 ClO^-(aq) \rightarrow ClO_3^-(aq) + 2 Cl^-(aq)$  is an example of **[IIT-2001]**

- (A) Oxidation reaction  
 (B) Reduction reaction  
 (C) Disproportionation reaction  
 (D) Decomposition reaction

**Sol.**

- Q.23**  $H_3PO_4$  and  $H_3PO_3$  is – **[IIT-2003]**

- (A)  $H_3PO_3$  is reducing agent and dibasic acid  
 (B)  $H_3PO_4$  is reducing agent and dibasic acid  
 (C)  $H_3PO_4$  is both reducing agent and tribasic acid  
 (D)  $H_3PO_3$  is not reducing agent and dibasic acid

**Sol.**

- Q.24** The acid having O–O bond is- **[IIT-2004]**

- (A)  $H_2S_2O_3$  (B)  $H_2S_2O_6$   
 (C)  $H_2S_2O_8$  (D)  $H_2S_4O_6$

**Sol.**

- Q.25** Which phosphorus is thermodynamically most stable ? **[IIT-2005]**

- (A) White (B) Red  
 (C) Black (D) Yellow

**Sol.**

- Q.26** When two gases are mixed at  $-30^\circ C$  the blue coloured gas is formed **[IIT-2005]**

- (A)  $N_2O_3$  (B)  $N_2$   
 (C)  $NO_2$  (D)  $N_2O_5$

**Sol.**

### Passage : (Q. 27 to 29)

The noble gases have closed-shell electronic configuration and are monoatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions.

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6.  $XeF_4$  reacts violently with water to give  $XeO_3$ . The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell.

- Q.27** Argon is used in arc welding because of its-  
(A) low reactivity with metal [IIT-2007]  
(B) ability to lower the melting point of metal  
(C) flammability  
(D) high calorific value

**Sol.**

- Q.28** The structure of  $\text{XeO}_3$  is -  
(A) linear (B) planar  
(C) pyramidal (D) T-shaped

**Sol.**

- Q.29**  $\text{XeF}_4$  and  $\text{XeF}_6$  are expected to be -  
(A) oxidizing (B) reducing  
(C) unreactive (D) strongly basic

**Sol.**

- Q.30** A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) H is (are)- [IIT-2008]

- (A)  $\text{NH}_4\text{NO}_3$  (B)  $\text{NH}_4\text{NO}_2$   
(C)  $\text{NH}_4\text{Cl}$  (D)  $(\text{NH}_4)_2\text{SO}_4$

**Sol.**

**Passage (Q.31 to Q.33)**

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of  $\text{NH}_3$  and  $\text{PH}_3$ . Phosphine is a flammable gas and is prepared from white phosphorous.

- Q.31** Among the following, the correct statement is-  
(A) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional  
(B) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional  
(C) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional  
(D) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional

**Sol.**

- Q.32** White phosphorus on reaction with NaOH gives  $\text{PH}_3$  as one of the products. This is a -  
 (A) dimerization reaction  
 (B) disproportionation reaction  
 (C) condensation reaction  
 (D) precipitation reaction

**Sol.**

- Q.33** Aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_3$  on reaction with  $\text{Cl}_2$  gives - **[IIT-2008]**  
 (A)  $\text{Na}_2\text{S}_4\text{O}_6$  (B)  $\text{NaHSO}_4$   
 (C)  $\text{NaCl}$  (D)  $\text{NaOH}$

**Sol.**

- Q.34** The reaction of  $\text{P}_4$  with X leads selectively to  $\text{P}_4\text{O}_6$ . The X is - **[IIT-2009]**  
 (A) Dry  $\text{O}_2$   
 (B) A mixture of  $\text{O}_2$  and  $\text{N}_2$   
 (C) Moist  $\text{O}_2$   
 (D)  $\text{O}_2$  in the presence of aqueous NaOH

**Sol.**

- Q.35** The nitrogen oxide(s) that contain(s) N-N bond(s) is (are) - **[IIT-2009]**  
 (A)  $\text{N}_2\text{O}$  (B)  $\text{N}_2\text{O}_3$   
 (C)  $\text{N}_2\text{O}_4$  (D)  $\text{N}_2\text{O}_5$

**Sol.**

- Q.36** Match each of reactions given in **Column I** with the corresponding product(s) given in **Column II** - **[IIT-2009]**
- | <b>Column I</b>                     | <b>Column II</b>               |
|-------------------------------------|--------------------------------|
| (A) $\text{Cu} + \text{dil HNO}_3$  | (p) $\text{NO}$                |
| (B) $\text{Cu} + \text{conc HNO}_3$ | (q) $\text{NO}_2$              |
| (C) $\text{Zn} + \text{dil HNO}_3$  | (r) $\text{N}_2\text{O}$       |
| (D) $\text{Zn} + \text{conc HNO}_3$ | (s) $\text{Cu}(\text{NO}_3)_2$ |
|                                     | (t) $\text{Zn}(\text{NO}_3)_2$ |

**Sol.**

- Q.37** The bond energy (in  $\text{kcal mol}^{-1}$ ) of a C-C single bond is approximately **[IIT-2010]**  
 (A) 1 (B) 10  
 (C) 100 (D) 1000

**Sol.**

**Q.38** All the compounds listed in Column I react with water. Match the result of the respective reactions with the appropriate options listed in Column II. **[IIT-2010]**

**Column I**

- (A)  $(\text{CH}_3)_2\text{SiCl}_2$   
formation  
(B)  $\text{XeF}_4$   
(C)  $\text{Cl}_2$   
(D)  $\text{VCl}_5$

**Column II**

- (p) Hydrogen halide  
(q) Redox reaction  
(r) Reacts with glass  
(s) Polymerization  
(t)  $\text{O}_2$  formation

**Sol.**

**Q.39** Extra pure  $\text{N}_2$  can be obtained by heating- **[IIT-2011]**

- (A)  $\text{NH}_3$  with  $\text{CuO}$  (B)  $\text{NH}_4\text{NO}_3$   
(C)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (D)  $\text{Ba}(\text{N}_3)_2$

**Sol.**

**Q.40** The reaction of white phosphorus with aqueous  $\text{NaOH}$  gives phosphine along with another phosphorus containing compound. The reaction type ; the oxidation states of phosphorus phosphine and the other product are respectively

- (A) redox reaction ; -3 and -5 **[IIT-2012]**  
(B) redox reaction ; +3 and +5  
(C) disproportionation reaction ; -3 and +5  
(D) disproportionation reaction ; -3 and +3

**Sol.**

# Answers

## Exercise-I

1. D	2. B	3. C	4. B	5. A	6. B	7. B
8. D	9. C	10. B	11. A	12. B	13. A	14. A
15. A	16. B	17. B	18. A	19. B	20. A	21. B
22. A	23. B	24. A	25. B	26. D	27. B	28. B
29. A	30. A	31. A	32. C	33. B	34. B	35. D
36. B	37. C	38. B	39. B	40. D	41. B	42. D
43. A	44. A	45. B	46. B	47. D	48. C	49. B
50. A						

## Exercise-II

1. D	2. C	3. B	4. B	5. C	6. A	7. C
8. A	9. B	10. A	11. A	12. D	13. A	14. A
15. B	16. C	17. A	18. C	19. C	20. A	21. A
22. C	23. C	24. B	25. B	26. C	27. A	28. A
29. B	30. A	31. A	32. D	33. A	34. A	35. B
36. C	37. A	38. C	39. C	40. A	41. A	42. D
43. A	44. A	45. B	46. C	47. A	48. C	49. C
50. B						

## Exercise-III

1. BC	2. BC	3. CD	4. ABC	5. AD	6. ABD	7. ABD
8. ABD	9. CD	10. AB	11. ABD	12. ABD	13. AB	14. BC
15. CD	16. AD	17. ABD	18. ABC	19. ABD	20. ABC	21. A
22. ABC	23. ABC	24. ABCD	25. B	26. C	27. A	28. B
29. B	30. D	31. C	32. A	33. B	34. D	35. A
36. C	37. B	38. A-R, B-P, C-T, D-S, E-Q	39. A-PS, B-QS, C-RT, D-QT,			
40. A-V, B-T, C-W, D-P, E-R, F-S, G-Q, H-U	41. A-T, B-S, C-P, D-Q, E-R, F-U					
42. A	43. C	44. E	45. E	46. A	47. A	48. B
49. C	50. B					

## Exercise-IV

### Level -I

Q.No.	1	2	3	4	5	6	7	8	9
Ans.	A	D	A	C	C	D	B	C	D

### Level -II

Q.No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Ans.	A	D	D	A	B	C	B	C	C	C	A	B	D	C	A	C	C	A	D	C	A	C	A
Q.No.	24	25	26	27	28	29	30	31	32	33	34	35	36										
Ans.	C	C	A	A	C	A	A, B	C	B	C	B	A, B, C	(A) $\rightarrow$ p, s ; (B) $\rightarrow$ q, s ; (C) $\rightarrow$ r, t ; (D) $\rightarrow$ q, t										
Q.No.	37	38										39	40										
Ans.	C	(A) $\rightarrow$ p, s ; (B) $\rightarrow$ p, q, r, t ; (C) $\rightarrow$ p, q, t ; (D) $\rightarrow$ p										D	C										